

STANDARDS DEVELOPMENT BRANCH OMIE



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OUTLINE OF ANALYTICAL METHODS

A guide to the occurrence,
significance, sampling and analysis
of chemical parameters
in water

March 7, 1974

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Ontario

Ministry
of the
Environment

The Honourable
William G. Newman,
Minister

Everett Biggs,
Deputy Minister

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OUTLINES OF ANALYTICAL METHODS

A guide to the occurrence, significance,
sampling and analysis of chemical parameters in water.

ONTARIO MINISTRY OF THE ENVIRONMENT

LABORATORY BRANCH

MARCH 7, 1974

FOREWARD

Information on analytical methods is often required in order to correctly interpret data and in the preparation of reports. This collection of analytical outlines has been prepared in order to provide pertinent information in a brief non-technical form so that the sampler will better be able to understand the meaning behind certain chemical parameters as well as their limitations. The outlines are not intended to be guides for performing the analyses.

Methods in this manual are specific for routine chemical analysis on water samples only and include specific instructions as to proper sampling and preservation techniques. Information regarding other tests can be obtained by contacting the Laboratories Branch, Ontario Ministry of the Environment.

Individual test descriptions will be revised periodically as needed. Samplers are urged to fill out the appropriate form at the back of this manual so that they can be notified as quickly as possible whenever changes take place.

INTRODUCTION

The Water Quality and Environmental Trace Contaminants Sections of the Laboratory Branch are equipped to do all standard chemical analyses on domestic water supplies, surface waters, ground waters, domestic wastes and industrial wastes. Special analyses required for research studies and unique pollution problems can also be provided but are not included in the context of this manual.

The main chemical laboratories are located in Toronto with regional laboratories now in operation at London and Thunder Bay. Mobile laboratories and field stations are used in conjunction with major surveys in areas remote from the regular laboratories.

SAMPLING

The method of collecting the sample in the field is the concern of the individual in charge of the particular survey; however, care must be taken to prevent contamination by sampling devices, motor exhaust, disturbing the bottom, etc. Water samples are normally placed in 20, 32, or 40 ounce glass bottles, although plastic bottles must be used for tests which are adversely affected by contact with glass. Specific sampling information is provided in each method summary. If there are any questions, it is in the best interest of the sampler to consult with laboratory staff before the samples are collected.

Sludge samples should be collected in wide mouth glass bottles and never filled more than half way. Bottles containing too much sludge may explode during shipping or when opened for the first time at the laboratory.

Follow the directions in the individual method outlines for proper preservation. Some parameters are stabilized by a certain preservation technique while others may be completely altered or destroyed. Be sure that the preservation technique is consistent with the tests requested.

Samples submitted for heavy metals are generally preserved with 10 drops of nitric acid per plastic bottle. Always add the acid after the sample is in the bottle. Never add acid to an empty plastic bottle prior to sampling. Strong acid will activate the plastic sides much like an ion exchange resin thereby enabling the container to retain various metals. Avoid the use of foil lined caps as these will decompose and contaminate the samples with extraneous metals.

SAMPLE VOLUMES

Each method outline specifies the minimum volume of sample required for proper analysis on all sample types. For the great majority of tests, however, the volume required is dependent on sample strength, with 'weaker' or clean samples

(e.g. domestic water supplies, well waters, and unpolluted surface waters) requiring the largest volumes. For a sample containing low concentrations of a substance, the largest practical volume is tested in order to obtain a sufficient quantity of the substance to detect reliably. For stronger samples such as effluents and sewages, a smaller amount, or even a dilution can often be employed.

In many instances samplers do not provide a sufficient quantity of sample to complete all the requested analyses. This is extremely frustrating to both the sampler who finds half of his analyses marked "SAMPLE EXHAUSTED", as well as the laboratory technician who spends 15 minutes of his time hunting down an empty bottle. There is sufficient information provided in this manual so that the sampler is well advised as to how much sample should be submitted. When circumstances arise in which the sampler does not feel that there is a sufficient volume of sample for all his requested analyses and it is impossible to acquire more sample, consultation with laboratory staff is recommended. This will enable the laboratory to assess his specific requirements and thereby make the best use of the available sample volume.

It is advantageous to have a remnant of the sample available after all tests have initially been set up. Samplers are therefore asked to submit at least 6 ounces of sample in excess of their original estimate. If the volume of sample chosen for a test is discovered to have been inappropriate to the strength of the sample, the test can then be repeated using a more informed choice of test volume. In addition, following completion of all tests, the results are reviewed to detect any calculation errors, uncertainty as to the composition, etc. It is of great assistance to have sufficient sample left to provide visual confirmation of its quality in comparison with the results obtained.

The best way to estimate the total required volume of sample is to sum the specified individual volumes for each test plus the extra 6 ounces discussed above. A number of tests, however, may be determined simultaneously on the same aliquot, therefore samplers should consider the following criteria before deciding on a total volume.

- 1) Both total phosphorus and Kjeldahl nitrogen can be determined on a single 75 ml. (3 ounce) aliquot.
- 2) Both sodium and potassium can be determined on a single 40 ml. (2 ounce) aliquot.
- 3) Nitrate nitrogen, nitrite nitrogen, free ammonia (ammonia nitrogen) and dissolved orthophosphate can all be determined on a single 75 ml. (3 ounce) aliquot.

- 4) Aluminum, copper, cadmium, cobalt, chromium, iron, lithium, molybdenum, manganese, nickel, silver, strontium, and zinc can all be determined on a single 400 ml. (14 ounce) aliquot. For very low levels, preconcentration necessitates that one full container (900 mls) be submitted for metals.

PERISHABILITY

The concentrations of almost all components undergo some changes with time after collection. This may be due to biological activity in the sample, chemical precipitation, adsorption or desorption with the walls of the container, chemical reaction between constituents, and volatility. Tests such as dissolved oxygen, dissolved carbon dioxide, free chlorine, and pH are examples of perishable parameters. Field analysis is recommended whenever possible. Detailed discussions as to perishability are provided in the individual method outlines where applicable.

SAMPLE SUBMISSION FORMS

When the sample is sent to the laboratory, a detailed description of known constituents should be included on the submission sheet, particularly if there is an unusual one, such as an industrial waste in a water sample. Most of the tests are subject to interferences (reactions which produce false results), when substances other than the one being measured react in a similar manner. Very often, these effects can be eliminated or reduced by taking proper precautions; however, it requires that the sampler give prior indication of possible contaminants. For example, a BOD determination is often meaningless if the sample contains material toxic to bacteria. If no warning is given, then the test will be carried out normally and an incorrect result will be reported.

If a group of related samples is submitted, a map of the area, or some indication of the location of waste inputs, is very helpful to the laboratory staff. It is also a good practice to number the samples in some logical order, such as downstream in a river. All analyses are examined before being released and an anomalous result might be improperly rejected, whereas some details as to the location would confirm its validity.

The exact analyses required must be stated. Samples cannot be accepted with such requests as "chemical analysis" or "all the metals". If there is doubt as to what analyses to request, a brief description of the purpose of collecting the sample will enable the laboratory staff to choose the appropriate tests. Samplers should always provide their telephone number or the telephone number of someone responsible for their samples. This will facilitate sample processing in case any uncertainties arise regarding instructions on the submission forms.

For unusual analyses, particularly those of industrial origin, an indication should be given as to whether quantitative or qualitative results are required. For the protection of the analyst, samples containing cyanide, arsenic, mercury or other toxic materials should be clearly marked.

Requests for analysis of extremely low concentrations of heavy metals, i.e. levels lower than shown as the detection limit in the individual outlines, should be clearly labelled "FOR PRECONCENTRATION" both on the submission sheet as well as on the sample bottle itself.

Samples which are non-homogeneous are difficult to analyze since it is virtually impossible to take a representative aliquot. For such samples, specific instructions should be provided as to whether analysis is required on the combined aqueous and suspended material, the aqueous phase alone, the suspended material alone, the organic phase alone (e.g. an oil slick), etc. The laboratory cannot take the responsibility of guessing correctly what the sampler desired from his samples, especially if the purpose of the analysis is not stated and there is no sufficient background data available.

Identification of unknown contaminants is very time consuming. Samples should be as large as possible to allow the necessary range of tests to be carried out. Information as to the source, the possible contaminants, and the industries implicated is extremely useful to the analyst.

Many hundreds of pesticide formulations are in use today, therefore, it is impossible to scan a sample for all of these. Compounds should be requested by name, or if this is not possible, by chemical class i.e. chlorinated hydrocarbons, carbamates, 2,4D herbicides, organophosphates etc.

Since chemical tests are divided among the Water Quality Section and the Environmental Trace Contaminant Section, sample processing becomes more efficient if separate sample submission forms and separate sample containers are used for the category of tests performed by each section. Fortunately the preservation requirements for these categories conveniently divide the two sections anyway. Therefore, in most cases this request is already being met and should present little additional inconvenience to the sampler. In cases where the same test is performed by both sections, the sample type is the deciding criteria as to which section performs the analysis. Generally clean surface waters, ground waters and domestic supplies are analyzed by the Water Quality Section while industrial waste and difficult domestic waste samples are analyzed by the Environmental Trace Contaminant Section. The following is a list of the chemical tests performed by each section.

<u>Water Quality Section</u>	<u>Environmental Trace Contaminant Section</u>	<u>Both Sections</u>
Acidity	Aluminum	Calcium
Alkalinity	Arsenic	Iron
Anionic Detergents (MBAS)	Barium	Magnesium
BOD ₅	Boron	Phenols
Carbon	Cadmium	Sulfide
Carbon Dioxide	Chromium	
Chloride	Cobalt	
Chlorophyll	Copper	
COD	Cyanide	
Color	Lead	
Dissolved Orthophosphate	Lithium	
Dissolved Reactive Silicates	Manganese	
Dissolved Solids	Mercury	
Fluoride	Molybdenum	
Free Ammonia	Nickel	
Hardness	Nitritotriacetic Acid (N.T.A.)	
Ignited Solids	Pesticides	
Nitrate Nitrogen	Petroleum Hydrocarbons	
Nitrite Nitrogen	Selenium	
pH	Silver	
Potassium	Solvent Extractables	
Settleability	Strontium	
Sludge Volume Index	Tannins and Lignins	
Sodium	Titanium	
Specific Conductance	Uranium	
Sulfate	Vanadium	
Suspended Solids	Zinc	
Total Kjeldahl Nitrogen		
Total Phosphorus		
Turbidity		
Volatile Acids		

SHIPPING PROCEDURES

A special appendix is being published separately.

PRECISION

Precision is a measurement which defines the error associated with a particular analytical method. When used in the context of this manual, precision refers to the standard deviation between multiple analyses on a single sample. The interpretive value of analytical data is greatly dependent upon precision since it is the fundamental criteria for distinguishing between real changes in water chemistry and analytical variability.

DETECTION LIMIT

The detection limit is the value below which one is unable to confirm a positive response for a particular chemical parameter. No chemical method is ever sensitive enough to confirm that nothing is there. Samplers are urged to be extra cautious in interpreting data which is very close to the defined detection limit, since analytical variability becomes large relative to the amount being measured.

RANGE OF APPLICATION

The range of application described in each method has been chosen to accommodate the majority of samples in a routine manner. It is not necessarily a definitive limitation on an analytical technique. Samplers should consult with laboratory staff regarding individual requirements since in some cases, the specified range may be extended to lower levels.

TIME OF ANALYSIS

The time of analysis defines the average number of tests per day possible with present facilities and could only be increased by reassigning staff deducted from other analytical functions. This number provides a guideline which will allow individual samplers to regulate their sample inputs so as to avoid pre-empting a large proportion of the daily capacity for any given test.

INQUIRIES

All chemical samples received by the Laboratory Branch are assigned numerical codes according to sample type. When the analyses are completed, the results are entered onto the original submission sheets, checked by the chemist-in-charge, and sent for typing. All original submission sheets are retained in the sample reception files. Laboratory staff are prepared to answer questions regarding the receipt and progress of samples but require the following information.

- 1) Municipality or Township in which the sample source is located.
- 2) Name of engineer, biologist, etc., responsible for the data.

- 3) Name of programme or study.
- 4) Sampling date and estimated date of arrival at the laboratory.
- 5) Location codes or other sample identification number. Laboratory numbers are preferred if known.
- 6) Type of sample (Water, River, Sewage, Industrial Wastes, Great Lakes, etc.).

A listing of appropriate telephone numbers is being published separately.

SUMMARY

CHEMICAL PARAMETER	PREFERRED SAMPLING CONTAINER	PRESERVATION TECHNIQUE	MINIMUM VOLUME OF SAMPLE (mls)	DETECTION LIMIT (IN mg/l UNLESS INDICATED)	ANALYTICAL METHOD
ACIDITY	Glass or Plastic	None Required	50	2	Titrimetric
ALKALINITY	Glass or Plastic	None Required	50	5	Titrimetric (Auto.)
ALUMINUM	Plastic	HNO ₃ (10 Drops/Bottle)	100	0.1, .02*	A.A.S.† Colorimetric
AMMONIA NITROGEN	- See Free Ammonia				
ANIONIC DETERGENTS (MBAS)	Glass	Refrigerate	100	0.1	Colorimetric
ARSENIC	Plastic or Glass	None Required	50	.01	Colorimetric
BARIUM	Plastic	HNO ₃ (10 Drops/Bottle)	100	0.2	A.A.S.†
BOD ₅	Glass	Refrigerate	500	0.2	Polarographic
BORON	Plastic Only	None Required	100	.02	Colorimetric
CADMIUM	Plastic	HNO ₃ (10 Drops/Bottle)	100	.02	A.A.S.†
CALCIUM	Glass or Plastic	None Required*	100	3, .05*	Titrimetric, A.A.S.†
CARBON	Glass or Plastic	Refrigerate	50	1	Colorimetric (Infrared)
CARBON DIOXIDE	Special*	Refrigerate*	*	0.5	Titrimetric
CHLORIDE	Glass	None Required	50	1*	Titrimetric (Auto)
CHLORINATED HYDROCARBONS	- See Pesticides				
CHLOROPHYLL	Field Filtration*	10% MgCO ₃ (1 ml/l)	1000	1 µg/l	Colorimetric
CHROMIUM	Plastic	HNO ₃ (10 Drops/Bottle)	100	.02	A.A.S.†, Colorimetric
COBALT	Plastic	HNO ₃ (10 Drops/Bottle)	100	.07	A.A.S.†
COD	Glass	Refrigerate	25	20	Titrimetric
COLOR	Glass	None Required	50	5 H.U.	Colorimetric (Visual)
CONDUCTIVITY	- See Specific Conductance				
COPPER	Plastic	HNO ₃ (10 Drops/Bottle)	100	.02	A.A.S.†
CYANIDE	Glass or Plastic	50% NaOH (1 ml/Bottle)*	500	.01, 1*	Colorimetric, Titrimetric
DISSOLVED ORTHOPHOSPHATE	Glass or Plastic	Refrigerate or Freeze	75	.002	Colorimetric (Auto.)
DISSOLVED REACTIVE SILICATES	Plastic Only	None Required	60	0.1	Colorimetric
DISSOLVED SOLIDS	Glass	None Required	75	50	Electrometric, Gravimetric
ETHER SOLUBLES	- See Solvent Extractables				
FLUORIDE	Glass or Plastic	None Required	350	0.1	Colorimetric (Visual)
FREE AMMONIA	Glass or Plastic	Refrigerate or Freeze	75	.02	Colorimetric (Auto.)
HARDNESS	Glass or Plastic	None Required	50	6	Titrimetric
HYDROCARBONS	- See Petroleum Hydrocarbons and Pesticides				
IGNITED SOLIDS	Glass	Refrigerate	*	100	Gravimetric
IRON (TOTAL)	Glass or Plastic*	HCl or HNO ₃ (10 Drops/Bottle)*	100	.05, .06*	Colorimetric (Auto.), A.A.S.†
KJELDAHL NITROGEN	- See Total Kjeldahl Nitrogen				
LEAD	Plastic	HNO ₃ (10 Drops/Bottle)	100	.07	A.A.S.†
LITHIUM	Plastic	HNO ₃ (10 Drops/Bottle)	100	.02	A.A.S.†
MAGNESIUM	Glass or Plastic	None Required*	100	.004*	A.A.S.†, Calculated
MANGANESE	Plastic	HNO ₃ (10 Drops/Bottle)	100	.04	A.A.S.†
MERCURY	Glass Only*	HNO ₃ - KMnO ₄ *	250	.05 µg/l	Flameless A.A.S.†

CHEMICAL PARAMETER	PREFERRED SAMPLING CONTAINER	PRESERVATION TECHNIQUE	MINIMUM VOLUME OF SAMPLE (mls)	DETECTION LIMIT (IN mg/l UNLESS INDICATED)	ANALYTICAL METHOD
METHYLENE BLUE ACTIVE SUBSTANCES	- See Anionic Detergents				
MOLYBDENUM	Plastic	HNO ₃ (10 Drops/Bottle)	100	.03	A.A.S.†
NICKEL	Plastic	HNO ₃ (10 Drops/Bottle)	100	.07	A.A.S.†
NITRATE NITROGEN	Glass or Plastic	Refrigerate or Freeze	75	.02	Colorimetric (Auto.)
NITRILOTRIACETIC ACID	Glass Only	Formaldehyde (2 mls/20 oz bottle)	600	.05	Polarographic
NITRITE NITROGEN	Glass or Plastic	Refrigerate or Freeze	75	.002	Colorimetric (Auto.)
NITROGEN	- See Ammonia, Total Kjeldahl, Nitrate, and Nitrite Nitrogen				
N.T.A.	- See Nitrilotriacetic Acid				
PESTICIDES	Glass Only*	Refrigerate*	1000	Variable*	Gas Chromatographic
PETROLEUM HYDROCARBONS	Glass Only*	Refrigerate*	900	Unspecified	Gas Chromatographic
pH	Glass or Plastic	None Required	25	0 pH Units	Potentiometric
PHENOLICS (REACTIVE)	Special*	Provided*	*	1 µg/l, 2 µg/l*	Colorimetric* (2 Types)
PHOSPHORUS	- See Total Phosphorus and Dissolved Orthophosphate				
POTASSIUM	Plastic*	None Required	40	0.1	Flame Photometric
SELENIUM	Plastic or Glass	HNO ₃ (10 Drops/Bottle)	100	.002	Fluorometric
SETTLABILITY	Glass	None Required	900	Unspecified	Volume Measurement
SILICA	- See Dissolved Reactive Silicates				
SILVER	Plastic	HNO ₃ (10 Drops/Bottle)	100	.04	A.A.S.†
SLUDGE VOLUME INDEX	None*	None Required	None*	Unspecified	Calculated
SODIUM	Plastic*	None Required	40	1	Flame Photometric
SOLIDS	- See Dissolved, Suspended and Ignited Solids				
SOLVENT EXTRACTABLES	Glass Only	Refrigerate	900	2	Gravimetric
SPECIFIC CONDUCTANCE	Glass	None Required	75	0.1 µmohs/cm	Electrometric
STRONTIUM	Plastic	HNO ₃ (10 Drops/Bottle)	100	.01	A.A.S.†
SULFATE	Glass or Plastic	None Required	50	1*	Colorimetric (Auto.)
SULFIDE	Glass or Plastic	Na ₂ CO ₃ -Zn(C ₂ H ₃ O ₂) ₂ , Refrigerate*	900	0.1, .02*	Colorimetric* (2 Types)
SUSPENDED SOLIDS	Glass	Refrigerate Only	200	5	Gravimetric
TANNINS AND LIGNINS	Glass	Refrigerate Only	200	1.0	Colorimetric
TITANIUM	Plastic	HNO ₃ (10 Drops/Bottle)	100	.02	Colorimetric
TOTAL KJELDAHL NITROGEN	Glass or Plastic	Refrigerate or Freeze*	75	0.1	Colorimetric (Auto.)
TOTAL PHOSPHORUS	Glass or Plastic	Refrigerate or Freeze*	75	.005	Colorimetric (Auto.)
TURBIDITY	Glass or Plastic	Keep in Darkness	50	0.5 FTU*	Nephelometric
URANIUM	Plastic	HNO ₃ (10 Drops/Bottle)	100	.01	Colorimetric
VANADIUM	Plastic	HNO ₃ (10 Drops/Bottle)	100	.04	Colorimetric
VOLATILE ACIDS	Glass	Refrigerate	25	50	Titrimetric
ZINC	Plastic	HNO ₃ (10 Drops/Bottle)	100	.05	A.A.S.†

* SEE INDIVIDUAL METHOD

† ATOMIC ABSORPTION SPECTROPHOTOMETRY

ACIDITY

The acidity of a water is a measure of its capacity to neutralize base. The major acidic component of natural waters is carbonic acid which is formed by the atmospheric absorption of carbon dioxide or by the release of carbon dioxide as a metabolic by-product. Under certain conditions, the presence of sulfuric acid, hydrochloric acid, and hydrolyzable metallic salts (primarily those of iron and aluminum) may provide for a "mineral acidity" in water. Drainage from mine tailings, for example, contains large amounts of sulfuric acid due to the aerobic oxidation of pyrite (iron sulfide) by sulfur bacteria as well as large amounts of hydrolyzable iron. The presence of a mineral acid is likely the result of industrial activity.

Carbonic acid acidity is present in any water that has a pH between 4.5 and 8.3. Mineral acidity predominates at pH levels below 4.5. Acid waters are objectionable because of their corrosive properties and their ability to inhibit biological activity.

Results for acidity are reported as mg/l of CaCO_3 . This represents the quantity of base, expressed as calcium carbonate, needed to increase the pH of a measured portion of a sample to 8.3. Acidity is best interpreted in conjunction with the pH and alkalinity, as well as any other appropriate analysis which would identify the acidic components of the water.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
50 mls (2 ounces)	GLASS OR PLASTIC	None Required (See Below)

Bottles should be filled completely so that no air bubbles remain after the sample is capped. Do not refrigerate as this may cause precipitation of calcium carbonate. Immediate delivery to the laboratory is essential.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
5 - 500 mg/l	5 mg/l (If pH >8.3 there is no Acidity)	± 2 mg/l

Samples are titrated manually with a standard sodium hydroxide solution (carbonate free) to a pH endpoint of 8.3 and the amount of titrant reported as a calcium carbonate equivalent.

Time of Analysis

Approximately 60 acidity determinations may be completed per day.

ALKALINITY

The alkalinity of a water is a measure of its capacity to neutralize acid. In neutral waters the main component of the alkalinity is the bicarbonate ion which may be formed by the action of dissolved carbon dioxide on limestone or other calcium type deposits. When the pH exceeds 8.3, carbonate and hydroxide ions also become components of the alkalinity.

The alkalinity of a water is generally used to define the buffering capacity or the water's capability to resist a change in pH. This means that if an acidic waste is discharged to a natural water system, the effect on the water may not necessarily be detected as a pH change, but will be detected as a drop in alkalinity.

Results for alkalinity are reported as mg/l of CaCO_3 . This does not necessarily imply that there is this much calcium carbonate in the water or that there is any at all. The alkalinity measurement represents the quantity of acid, expressed as calcium carbonate, needed to reduce the pH of a measured portion of sample to 4.5

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
50 mls (2 ounces)	GLASS OR PLASTIC	None Required (See Below)

Bottles should be filled completely so that no air bubbles remain after the sample is capped. Do not refrigerate as this may cause precipitation of calcium carbonate. Immediate delivery to the laboratory is essential.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
2 - 800 mg/l	2 mg/l (If pH < 4.5 there is no alkalinity)	± 1 mg/l

Samples are titrated automatically on a Titralyzer with a standard sulfuric acid solution to a pH endpoint of 4.5. The alkalinity is then reported as the amount of calcium carbonate required to react with the acid consumed in the titration.

Time of Analysis

Approximately 120 alkalinity determinations may be completed per day.

ALUMINUM

Aluminum is one of the most abundant elements in nature being widely distributed in both soluble and insoluble forms. Its most important sources are bauxite, cryolite, alum, corundum and kaolin minerals. Aluminum compounds occur naturally in water, but may also be derived from industrial wastes or water treatment plant effluents where it is commonly used as a precipitating or flocculating agent. The presence of small amounts of aluminum in water may interfere with certain industrial processes.

At present, there is no evidence that aluminum is physiologically harmful and no drinking water objective has been specified. Toxic effects on plants have been reported for extreme conditions at both ends of the pH scale, but at a neutral pH, toxicity effects are negligible.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
100 mls (4 ounces)	PLASTIC	HNO ₃ (10 Drops/Bottle)

NOTE: Do not use caps with foil liners.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
A.A.S. 0.1 - 1.0 mg/l	0.1 mg/l	± .02 mg/l
Colorimetric .02 - 0.5 mg/l	.02 mg/l	± .02 mg/l

Analysis may be accomplished by atomic absorption spectrophotometry using a nitrous oxide-acetylene flame or by the colorimetric aluminon method. Iron, phosphates, and fluoride interfere in the aluminon method. If such species are likely to be present in abundance, the laboratory should be notified.

Time of Analysis

Time of analysis depends on the amount of preparation work required. Approximately 32 analyses may be performed per day on undigested samples whereas 16 analyses may be performed per day on digested samples.

ANIONIC DETERGENTS
(Methylene Blue Active Substances)

Anionic detergents are generally sodium salts of complex organic compounds of the sulfate and sulphonate variety. All are readily soluble in water and ionize to produce the sodium cation and a negatively charged surface active organic ion. They are commonly referred to as "surfactants" because of their ability to reduce the surface tension of water.

Anionic detergents are not found in nature, therefore the presence of these substances in natural waters indicates contamination by domestic or industrial wastes. While generally considered non-toxic to most life forms at low levels, they are objectionable because they cause excessive foaming and inhibit the normal exchange of atmospheric oxygen with water.

The test for anionic detergents is more accurately referred to as "methylene blue active substances" (MBAS) since any material which forms a colored complex with methylene blue will be detected. The reported result most likely represents an overestimate of the anionic detergent concentration therefore caution should be exercised in interpreting the result. Samples which do not produce any foam when shaken, contain less than 0.5 mg/l of MBAS as LAS (Linear alkyl sulfonates). Since this is the objective for natural waters, it is not necessary to request a MBAS analysis on samples when a perceptible foam does not appear.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
100 mls (4 ounces)	GLASS	REFRIGERATE

MBAS are unstable and will be degraded rapidly by bacterial activity. Refrigeration is helpful and immediate delivery to the laboratory is essential. Care must be taken to avoid contamination of the sampling containers by any detergent product used for cleaning

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
0.1 - 0.5 mg/l	0.1 mg/l	± 0.1 mg/l

Samples are mixed with a methylene blue reagent and any substances in the sample which are methylene blue active will be extracted as blue colored salts in chloroform (they are more soluble in chloroform than in water). The chloroform layer is then analyzed colorimetrically using LAS as the calibration standard. Results are reported in mg/l of MBAS as LAS.

Time of Analysis

Approximately 36 MBAS analyses may be completed per day.

ARSENIC

Arsenic is commonly found in nature as the minerals realgar, orpiment, arsenolite, mispickel, and arsenopyrite. Arsenic is present in natural waters by dissolution of these minerals, industrial discharges, and insecticide application.

The element and its salts are highly toxic to humans and also have been identified as carcinogens. Since arsenic is eliminated only slowly from the body, it tends to accumulate, becoming concentrated in the nails and hair. Hence, the prolonged intake of water containing only minute quantities of arsenic may be detrimental to health. For this reason, the maximum permissible concentration in domestic water supplies has been established as 0.05 ppm, with an objective of less than 0.01 ppm.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
50 mls (2 ounces)	PLASTIC OR GLASS	NONE REQUIRED

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.01 - 1.0 mg/l	.01 mg/l	± .01 mg/l

In order to obtain the arsenic in a form suitable for analysis, the sample is first digested with a nitric-sulphuric acid mixture. Then the arsenic is reduced to arsine, AsH_3 , and reacted with silver diethyldithiocarbamate solution in a modified Gutzeit generator to form a coloured compound. The concentration of arsenic is then obtained colorimetrically. Several metals may interfere to a small extent with the generation of arsine, but the chief interference is antimony which will react with the colour reagent similarly to arsenic. Results are expressed as elemental arsenic.

Time of Analysis

Approximately fifteen arsenic analyses can be completed per day.

BARIUM

Barium is commonly found in nature as the minerals barite (barium sulfate) and witherite (barium carbonate). It is also found in igneous rock, primarily feldspar, where it is known to replace potassium. Barium is present in all soils usually at very low levels, but these naturally occurring substances are very insoluble in water. The presence of barium in water is very rare unless originating in an industrial discharge. Industrial application of barium includes the manufacture of metal alloys, paints, pigments, paper, soap, rubber, linoleum, flares, cement and various other products.

Insoluble barium salts are relatively non-toxic. Barium sulfate, for example, is used as a contrast material in the radiological diagnosis of ulcers. Soluble salts of barium, however, are readily absorbed through the skin or gastrointestinal tract and exhibit highly toxic effects on the nervous system if present in sufficient quantity. Symptoms include violent muscular spasms, paralysis and cardiac arrest. Trace quantities of soluble barium are known to accumulate in bones, but are not believed to exhibit a cumulative toxic effect like lead or cadmium. The maximum acceptable concentration of barium in a domestic water supply is 1.0 mg/l.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
100 mls (4 ounces)	PLASTIC	HNO ₃ (10 Drops/Bottle)

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.02 - 2.0 mg/l	0.2 mg/l	Presently Not Available

Samples are digested with a nitric-hydrochloric acid mixture and analysis is accomplished by atomic absorption spectrophotometry using a high temperature nitrous oxide-acetylene flame. Potassium nitrate is generally added to the sample to suppress the ionization of barium during analysis. The analysis is subject to several positive interferences which reduce the experimental precision.

Time of Analysis

Approximately 50 barium analyses may be completed per day.

BIOCHEMICAL OXYGEN DEMAND (BOD₅)

The most frequent damage caused by the discharge of wastes to natural waters, is the reduction of dissolved oxygen concentrations to levels which cannot support normal aquatic life. This oxygen depletion arises via the bacterial oxidation of organic material and eventually leads to a general deterioration of water quality for all uses.

The BOD₅ test is defined as the measure of dissolved oxygen required for the aerobic bacterial stabilization of decomposable organic matter in a five day period at 20°C in the absence of light. Ideally the BOD₅ should be supplemented by on-site dissolved oxygen measurements in order to assess the effects of stream conditions which offset or accentuate the utilization of dissolved oxygen.

The precision of the method is seriously reduced if the sample contains large fragments of suspended solids or an immiscible layer of oil. Representative portions of such samples cannot be properly aliquoted and the results are not generally reproducible to within acceptable limits.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
500 mls (18 ounces)	GLASS	REFRIGERATE

The BOD₅ is a perishable quantity since it is readily influenced by bacterial activity. Immediate delivery to the laboratory is essential.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
1 - 10 mg/l of Oxygen	0.2 mg/l of Oxygen	± 0.1 mg/l of Oxygen

Dilutions are prepared on the original sample as necessary, and the dissolved oxygen depletion measured after a five day incubation period in a sealed bottle at 20°C. Only those dilutions which give a dissolved oxygen depletion between 25 and 75% are accepted for calculating the BOD₅. Dissolved oxygen levels are measured on a dropping mercury polarograph which has been calibrated via the Winkler Method (1). Samples with high chlorine residuals and adverse pH levels are chemically adjusted to remove these toxic influences and are then seeded with sewage.

Time of Analysis

By definition, the BOD₅ test will take five days to complete, however, approximately 250 BOD₅ analyses may be set up per day.

BORON

Boron occurs in nature as the minerals borax, colemanite, boronatrocalcite, and boracite. It is used as a neutron absorber and shielding material in nuclear power plants, as a hardening constituent in steel alloys, as a fire proofing agent, and in the manufacture of glass, porcelain enamels, detergents, pharmaceuticals, abrasives, dyes and high energy fuels.

Boron is an essential trace element for plant growth, playing a significant role in respiratory processes and the breakdown of carbohydrates. No similar function has been discovered in animals.

Boron is toxic to both animals and plants at high concentrations. Symptoms of boron poisoning in humans include abdominal pain, nausea, and diarrhea. Death occurs as a result of central nervous system paralysis.

Although natural mineral deposits may significantly increase the boron concentration in water, it usually originates via the disposal of cleaning agents in urban sanitation systems or the discharge of industrial effluents. Boron is generally found as the borate anion and very seldom exceeds 0.1 mg/l.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
100 mls (4 ounces)	PLASTIC ONLY	NONE REQUIRED

Glass containers should not be used since boron is a major component of glass.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.02 - 1.0 mg/l	.02 mg/l	± .01 mg/l

Samples are acidified and evaporated to dryness in the presence of curcumin to produce a red coloured boron derivative known as rosocyanine. This material is dissolved in ethyl alcohol and analysis is accomplished colorimetrically. Nitrate concentrations in excess of 20 mg/l cause an interference.

Time of Analysis

Approximately 15 boron analyses may be completed per day.

CADMIUM

Cadmium and its salts are used in metallurgy, electroplating, pigment and insecticide preparation as well as in various other industrial applications. Its main natural source is the mineral greenockite which may contain up to 77% cadmium. All forms of this element are highly toxic, and once ingested, are likely to remain in the body for a long time, becoming concentrated in the liver, kidneys, and other organs. Cases have been reported where toxic effects did not become apparent until many years after the last exposure. Its presence in natural waters is usually a result of industrial discharges or by the deterioration of galvanized pipe. The drinking water objective for cadmium is 0.01 mg/l therefore a highly sensitive analytical method is required.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
100 mls (4 ounces)	PLASTIC	HNO ₃ (10 Drops/Bottle)

When levels below the normal range of application are required, a notation must be included on the sample submission form so that the sample may be preconcentrated prior to analysis. One full 32 oz. bottle is required exclusively for the preconcentration process.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.02 - 3.0 mg/l	.02 mg/l	± .008 mg/l (At the 0.1 Level)

Samples are digested using a mixture of nitric and sulfuric acid and then analyzed using atomic absorption spectrophotometry. Cadmium is one of the elements most suited to atomic absorption analysis as there are no known chemical or spectral interferences.

Time of Analysis

Approximately 50 cadmium analyses may be completed per day.

CALCIUM

Calcium ranks fifth in the order of natural elemental abundance and is commonly found in deposits of limestone, dolomite, gypsum, and gypsiferous shale. It is generally present in all natural waters at levels which depend on the amount of contact with specific geological formations. For this reason, surface water tends to be lower in calcium than ground water.

Calcium is an essential element for all life forms. In plants, it is known to enhance biological productivity; in animals, it is necessary for proper bone and teeth formation. Aqueous calcium compounds are generally non-toxic and represent no known health hazard.

Small concentrations of calcium assist in preventing the corrosion of metal pipes by forming a protective layer of calcium carbonate, however, large concentrations cause excessive scale which leads to restricted flow and pressure build-ups. Calcium is the major contributor to water "hardness", therefore the amount of calcium in water supplies is of concern, especially to industry (see hardness).

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
100 mls (4 ounces)	GLASS OR PLASTIC	None * Required

*Non-routine industrial waste samples, or any other samples where high levels of heavy metals are suspected, should be sampled in plastic containers and preserved with 10 drops of nitric acid per bottle.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
Titrimetric 3 - 200 mg/l	3 mg/l	± 1 mg/l
A.A.S. .05 - 5.0 mg/l	.05 mg/l	± .01 mg/l

Samples are buffered to a pH of 12-13 and titrated with ethylenediaminetetraacetic acid (EDTA) to the Murexide endpoint. Non-routine industrial waste samples, etc., are analyzed for calcium using atomic absorption spectrophotometry.

Time of Analysis

Approximately 70 calcium analyses may be completed per day using the titrimetric method and 50 per day using the atomic absorption method.

(Total, Organic and Inorganic)

Both total carbon and inorganic carbon are determined by direct analysis on a liquid sample. The organic carbon component is obtained by taking the difference between the total carbon and the inorganic carbon.

The total organic carbon result (TOC) will have a direct relationship with the BOD and COD value for samples with a constant organic composition. Just as the COD/BOD ratio indicates the degree of biodegradability, the COD/TOC ratio indicates the type of organic substances present.

Carbon analyses are rapid and relatively simple to perform. The TOC is often preferred to the BOD and COD because it relates more directly to the organic content of a water. It is commonly used to assess the efficiency of waste stabilization processes and the degree of organic pollution in receiving waters. Inorganic carbon results are essential in calculating the biological productivity of a water.

The presence of suspended solids in a water sample decreases the precision of the analysis. Only a supernatant analysis is performed unless otherwise requested.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
50 mls	GLASS OR PLASTIC	REFRIGERATE

Containers should be filled completely so that no air bubbles remain once the sample is capped. Production of CO₂ and interconversion of carbon forms via bacterial activity is likely, therefore immediate delivery to the laboratory is essential.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
1 - 100 mg/l	1 mg/l	± 1 mg/l

Total carbon is determined by injecting a known volume of sample onto a hot catalyst using a hypodermic syringe. The CO₂ gas produced on combustion is measured by infrared spectrophotometry. Inorganic carbon is determined by acidifying a known volume of sample in a closed chamber and the released CO₂ gas measured by infrared spectrophotometry. Results are reported in mg/l of carbon. Consult with laboratory staff if lower levels are required.

Time of Analysis

Approximately 60 carbon analyses may be completed per day.

CARBON DIOXIDE

Dissolved carbon dioxide (carbonic acid) is generally found in all water samples with a pH between 4.5 and 8.3. Surface water contains dissolved CO₂ as a result of atmospheric absorption. Ground waters and waters from the hypolimnion of stratified lakes and reservoirs contain dissolved CO₂ as a result of bacterial activity. Carbon dioxide is an endproduct of both aerobic and anaerobic bacterial oxidation and is not limited by the amount of dissolved oxygen.

The dissolved carbon dioxide determination has many sources of error, therefore caution must be exercised in its interpretation. It is an acidity measurement and will include all forms of acidity not only CO₂. Samples with a pH close to 4.5 may produce CO₂ results which are really the sum of the carbonic acid acidity and the mineral acidity. Any changes in temperature or barometric pressure are likely to change the CO₂ content of the sample.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
Full Special Container	Special Glass Bottle (See Below)	(See Below)

Special precautions are required to minimize agitation of the sample otherwise CO₂ will be lost. Samples are to be carefully transferred from the sampling device into the bottom of a special leak proof glass stoppered container via a syphon. Allow plenty of sample to overflow before the container is finally capped. If any air bubbles remain in the container, analysis cannot be performed. Samples should then be refrigerated and brought to the laboratory within 24 hours. Samplers generally deliver CO₂ samples personally as they are unsafe to ship commercially.

Consultation with laboratory staff is required prior to sampling as special preparations are necessary before the samples arrive. Field determinations are recommended when possible.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
0.5 - 88 mg/l	0.5 mg/l	± 0.5 mg/l

Samples are transferred by syphon to Nessler tubes where they are titrated potentiometrically with carbonate free sodium hydroxide to a pH endpoint of 8.3. Special precautions are practised to limit any errors due to atmospheric exchange of CO₂. Results are reported in mg/l of CO₂.

Time of Analysis

Approximately 40 CO₂ analyses may be completed per day.

CHEMICAL OXYGEN DEMAND (COD)

The chemical oxygen demand is a measure of the oxygen required to oxidize susceptible organic compounds under vigorous chemical oxidizing conditions. This test is especially useful on industrial wastes where the BOD₅ test is not applicable. Toxic materials in industrial wastes tend to inhibit bacterial activity producing a BOD₅ which generally underestimates the true organic composition of the sample. Most organic compounds are oxidized by the COD method; the most common exceptions are benzene, toluene, pyridine, and similar aromatic ring compounds. Ammonia and organic nitrogen do not react in this test.

COD results do not necessarily relate directly to the BOD₅ value or to the oxygen consumption in the receiving water, but they do represent the ultimate carbonaceous oxygen demand that may eventually be exerted. If a number of comparative analyses show that a stable ratio exists between the COD and BOD for a particular waste, then the COD results may be used to predict the approximate BOD values.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
25 mls (1 ounce)	GLASS	REFRIGERATE

The COD is a perishable quantity since it may be influenced by bacterial activity. Immediate delivery to the laboratory is essential.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
20 - 800 mg/l of Oxygen	20 mg/l of Oxygen	± 5 mg/l of Oxygen

A water sample is refluxed with a known amount of potassium dichromate and sulfuric acid for two hours. Mercuric sulfate is added to prevent chloride interference, and silver sulfate is added to catalyze the oxidation of straight chain hydrocarbons. The oxygen utilized by the sample is determined by titration with ferrous ammonium sulfate and results are reported in mg/l of oxygen.

Time of Analysis

Approximately 65 COD analyses may be completed per day.

CHLORIDE

Chloride is a major anion in domestic wastes and in many natural water supplies. Urban runoff often contains high concentrations of chloride in the winter time due to road application of salt.

Chloride poses no direct health hazard, but the water quality objective for domestic water supplies has been specified at 250 mg/l to prevent a salty taste. This salty taste is variable and dependent on the composition of the water. If chloride is present as sodium chloride, a detectable taste will be present at 250 mg/l. If chloride is present as calcium or magnesium chlorides, waters containing as much as 1000 mg/l may not have a noticeable taste.

The chloride method actually measures the total of chloride, bromide, iodide, and cyanide concentrations, therefore caution must be exercised in interpreting the chloride results. In the case of natural fresh waters, the concentrations of bromide, iodide, and cyanide are negligible and the result will closely represent the chloride content of the sample. In regions of Northern Ontario where watercourses are influenced by Arctic tidewater, this is not the case.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
50 mls (2 ounces)	GLASS	None Required

A low level method is presently available to extend the detection limit down to 0.05 mg/l. Applications include rain water analysis and special studies. Laboratory staff should be consulted if low level measurements are required.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
1 - 400 mg/l	1 mg/l	± 2 mg/l

Samples are titrated automatically on a Titralyzer instrument using a standardized silver nitrate solution. Sulfide, thio-sulfate, sulfite, and orthophosphate are known interferences when present in abundance.

Time of Analysis

Approximately 120 chloride analyses may be completed per day.

CHLOROPHYLL

Chlorophyll is the natural pigment component of all green plants. The quantity of chlorophyll in a water sample is therefore a good indication of how much plant material is present. More specifically, chlorophyll data provides a way to estimate the biomass of standing algae crops which can then be used to assess the effectiveness of nutrient removal programmes as well as the general trophic status of lakes and rivers.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
1000 mls (36 ounces)	None - Field Filtration is Recommended (See Below)	10% MgCO ₃ at 1 ml Per Liter of Sample

Add one milliliter of a 10% magnesium carbonate suspension to about one liter of sample. This prevents the conversion of chlorophyll to pheopigments at low pH levels. Do not add too much preservative as this may absorb some pigment. Filter a measured aliquot (approximately one liter) through a 1.2 micron cellulose nitrate membrane filter. Avoid a filter pressure in excess of 30 mm of Hg, as this may rupture phytoplankton cells with a subsequent loss of chlorophyll. Place the moist filter in a plastic petrie dish on top of a piece of regular filter paper in order to absorb excess moisture. Label the petrie dish and be sure to record the volume of the filtered aliquot. Wrap the petrie dishes tightly in aluminum foil and ship to the laboratory for analysis.

If filtration in the field is not possible, efforts must be made to retard photosynthetic activity. Sample should be taken in glass bottles, refrigerated and kept in the dark. Immediate delivery to the laboratory is essential.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
2 - 8 µg/l	1 µg/l	Presently Not Available

Chlorophyll is extracted with 90% acetone and analysis accomplished spectrophotometrically at four different wavelengths. The equations of Richards and Thompson are then used to calculate the chlorophyll a and b concentrations using this spectrophotometric data. Blank corrections for turbidity are applied if necessary. Any other pigments or degradation products which absorb at the analysis wavelengths are detected as interferences.

Time of Analysis

Approximately 100 chlorophyll analyses may be completed per day.

CHROMIUM

Hexavalent chromium salts are used extensively in the plating industries, tanneries, and in the manufacture of paints and dyes. Industrial uses for trivalent chromium are more limited. The presence of chromium in water will probably be the result of one of these industrial discharges or the result of the discharge of cooling waters in which chromium has been used as a corrosion inhibitor.

Chromium is present in small quantities in all soils and plants, but there is no evidence to indicate that it is required by plants for growth. It occurs in nature primarily as chromite or chrome iron ore. Soils with a high chromium content are generally infertile. Hexavalent chrome is the more toxic form of the element exhibiting carcinogenic properties. The maximum permissible concentration in domestic water supplies has been established at 0.05 mg/l.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
100 mls (4 ounces)	PLASTIC	HNO ₃ (10 Drops/Bottle) No Preservative for Hexavalent Chrome

NOTE: Fill bottle completely to the top and deliver to the laboratory as quickly as possible. Chromate ion is readily adsorbed on container surfaces and delays in shipment longer than 2 to 3 days may cause erroneous results.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
A.A.S. .02 - 2.0 mg/l	.02 mg/l	± .02 mg/l
Colorimetric .02 - 20 mg/l	.02 mg/l	± .02 mg/l

For a total chromium analysis, the sample must first be digested with sulphuric and nitric acids and hydrogen peroxide; then the chromium is oxidized with permanganate to the hexavalent form. Once in this form, the chromium concentration can be determined by the colorimetric diphenylcarbazide method or by atomic absorption spectrophotometry. Hexavalent chromium is determined directly by the diphenylcarbazide method with no sample pretreatment other than filtration. High levels of chloride, vanadium, iron, and mercury are known to interfere with the colorimetric method.

Time of Analysis

Approximately 18 chromium analyses may be completed per day by either the colorimetric or atomic absorption methods when analyzed in batches. More hexavalent chrome determinations may be performed per day because of the minimum amount of preparation required.

COBALT

Cobalt is found in nature as the minerals cobalite, smaltite, and erythrite. It is widely used in the manufacture of alloys and pigments used in glass staining. Recently, it has found use as a binder in the tungsten carbide tool industry where it is commonly added to steel as a means of improving the cutting quality of certain tools.

Cobalt is an essential element at trace levels for both animal and plant nutrition. It is known to be one of the main constituents of Vitamin B₁₂ and its presence is believed to be instrumental in the natural synthesis of this vitamin. Cobalt deficiency in man and animals results in a type of anaemia which may be corrected by administering small dosages of cobalt chloride orally. Adverse effects due to cobalt are very slight even at high concentrations. Nausea and diarrhea are the common symptoms. No limits have been set on the maximum acceptable concentration for cobalt in domestic water supplies. Tentative limits suggested by the Water Quality Criteria are 0.2 mg/l for continuous irrigation of all soils and 10 mg/l for short term use on fine textured soils.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
100 mls (4 ounces)	PLASTIC	HNO ₃ (10 Drops/Bottle)

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.07 - 7 mg/l	.07 mg/l	± .01 mg/l

Samples are digested with a nitric-sulfuric acid mixture and analysis is accomplished using atomic absorption spectrophotometry.

Time of Analysis

Approximately 50 cobalt analyses may be completed per day.

COLOR

Many lakes and rivers, especially in Northern Ontario, have a characteristic yellowish-brown color due to the presence of humic acids derived from the decomposition of plants. Lakes of this type are commonly referred to as "acid bog" or "brown water" lakes. A similar color may also occur when iron and manganese are found in abundance.

Water colored naturally by humic substances is harmless, but considered unacceptable for drinking purposes because of its appearance. The objective of 5 color units for domestic water supplies is therefore based on aesthetic rather than on health standards. Waters with color differing in hue from that of natural waters such as those of industrial origin cannot be measured by this method. Consultation with laboratory staff may allow other relevant tests to be chosen.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
50 mls (2 ounces)	GLASS	None Required

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
5 - 60 H.U.	5 H.U.	± 5 H.U.

The sample is compared to a series of standard color disks of matching hue which are calibrated in Hazen Units, H.U. (derived from the originator's name). The comparison is made in an optical instrument called the Lovibond Color Comparator. "Apparent color" which includes both the "true color" present in solution and the additional color contributed by suspended matter is normally reported unless otherwise indicated.

Time of Analysis

Approximately 100 color analyses may be completed per day.

COPPER

Copper occurs naturally as the free native metal as well as in malachite, cuprite, chalcopyrite and various mixtures of sulfide ores. Copper salts in natural water generally originate in the effluents of a wide variety of industries, but they are also used in controlling the growth of algae which occur as objectionable slimes in reservoirs and water distribution systems.

Copper is an essential element to the human body, acting as a catalyst in many biochemical reactions. It is generally agreed that copper is an active agent in the synthesis of hemoglobin and that a copper deficiency in animals causes a severe anaemia similar to iron deficiency anaemia. A daily intake of about 2 mg is required for normal body functions. Excessive amounts of copper are toxic, and cause abdominal pain, vomiting and convulsions. Prolonged exposure results in liver and kidney damage. Copper imparts a disagreeable taste to water at concentrations well below those which would be hazardous to health, hence the drinking water objective of 1.0 mg/l is based on taste rather than on toxicity.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
100 mls (4 ounces)	PLASTIC	HNO ₃ (10 Drops/Bottle)

Do not acidify the sample if both dissolved and suspended forms are to be determined.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.05 - 5 mg/l	.02 mg/l	± .015 mg/l (At the 0.3 Level)

Samples are first digested with nitric and sulfuric acid and then analyzed using atomic absorption spectrophotometry. High concentrations of sodium and/or potassium (0.5%) interfere with the copper analysis. Laboratory staff should be warned if such concentrations are suspected.

Time of Analysis

Approximately 50 copper analyses can be completed per day.

CYANIDE

Cyanides are a class of chemical compounds which contain a carbon-nitrogen constituent commonly referred to as the cyanide group. Cyanides vary in their degree of chemical activity depending on how readily they dissociate in water to form the cyanide ion. Simple cyanides of the alkali metals readily form this ion while many metal cyanides do so at a much slower rate or not at all.

The presence of cyanide in natural waters is the result of an industrial discharge. Waters containing this substance are extremely toxic to virtually all aquatic life forms and are unsafe for human consumption. Cyanide exerts its toxic effects by inhibiting the normal oxidation processes in body tissue thus causing asphyxiation and death. The maximum acceptable cyanide concentration for domestic water supplies in Ontario has been set at 0.01 mg/l of cyanide as HCN.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
500 mls (18 ounces)	GLASS OR PLASTIC	1 ml of 50% NaOH Per Bottle REFRIGERATE

A sample suspected of containing cyanide should never be acidified, as this will release highly toxic cyanogen gas.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
Colorimetric .01 - 1.0 mg/l	.01 mg/l	± .01 mg/l
Titrimetric 1 - 50 mg/l	1 mg/l	± 1 mg/l

All samples are distilled prior to analysis to remove interferences. If an analysis for the ionic or "free cyanide" is required, the sample is distilled from a weakly acidic tartaric acid solution. If a "total cyanide" analysis is required, the sample is distilled under reflux from a solution containing strong acid and metal salts (Serfass Distillation). Samples with more than 1 mg/l of HCN are determined titrimetrically using silver nitrate, while samples with less than 1 mg/l of HCN are determined colorimetrically using chloramine-T and a pyridine-pyrazolone reagent. Results are reported in mg/l of HCN.

Time of Analysis

Approximately 16 "free cyanide" analyses may be completed per day, while only 2 "total cyanide" analyses may be completed per day.

DISSOLVED ORTHOPHOSPHATE

The dissolved orthophosphate content of a sample is that fraction which passes through a filter and reacts during analysis to produce a positive colorimetric response. It is generally accepted that some organic and even particulate forms of orthophosphate can react similarly to dissolved orthophosphate and for this reason, the results are often referred to as "dissolved reactive orthophosphate", which removes the implication that the test measures only the orthophosphate forms which are uncombined and in solution.

Phosphorus is an essential element for all life forms. Artificial inputs of phosphorus via wastewater and land run-off plays a significant role in promoting the overabundance of algae and aquatic plants which may impair water quality. However, the usefulness of the dissolved orthophosphate result is questionable because of the ion's extreme reactivity. Results must be interpreted with full allowance for its perishability, both in situ and in the sample following collection.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
75 mls (3 ounces)	GLASS OR PLASTIC	REFRIGERATE OR FREEZE

Dissolved orthophosphate is extremely perishable. Samples must be refrigerated or frozen immediately after collection and delivered to the laboratory as soon as possible. A rinse with 10% hydrochloric acid and distilled water is recommended to remove any possible phosphorus contamination from sampling containers.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.002 - 0.2 mg/l	.002 mg/l	± .001 mg/l

Samples are pretreated by filtration and analysis accomplished colorimetrically using the phosphomolybdate method which has been adapted to an Auto Analyzer system. High levels of silica, iron, trivalent chrome, hexavalent chrome, copper, zinc, and various oxidizing agents are known to cause interferences. Results are reported in mg/l of phosphorus.

Time of Analysis

Approximately 200 analyses may be completed during an 18 hour Auto Analyzer working period.

DISSOLVED REACTIVE SILICATE

The element silicon ranks second to oxygen in abundance and is present as silica or silicates in sand or quartz. Its presence is essential to the growth of diatoms as well as many other aquatic organisms. Silicates are non-toxic and no maximum concentration has been specified for its presence in domestic water supplies.

Silicates are widely used in industry for the manufacture of glass, ceramics, abrasives and enamels and have been used in domestic water treatment as coagulants, corrosion inhibitors, and sequestering agents for iron. Their presence in boiler feed waters causes deposits of silica on steam-turbine blades, necessitating removal to concentrations as low as 0.1 mg/l in high pressure systems.

The test is often improperly referred to as a "SILICA" analysis, but in actuality silica is not measured. Silica (SiO_2) is an extremely inert and insoluble substance which will not be detected under the conditions of this test. Only silicate salts and polymeric silicates referred to as "DISSOLVED REACTIVE SILICATE" are detected. In order to be consistent with the units of other environmental agencies, results are reported as SiO_2 , but this is not the form that has been analyzed.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
60 mls (3 ounces)	PLASTIC ONLY	None Required

Glass bottles should not be used since silicon is a major constituent of glass.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
0.1 - 6 mg/l	0.1 mg/l	± 0.1 mg/l

Samples are analyzed directly using the colorimetric molybdate method. Results are reported in mg/l as SiO_2 . Iron, color, turbidity, tannins, sulfides, and phosphates in abundance are potential interferences.

Time of Analysis

Approximately 80 silicate analyses may be completed per day.

DISSOLVED SOLIDS

Dissolved solids refers to the quantity of material that remains as a residue after the water is removed from a filtered portion of sample by evaporation. The test does not determine specific chemical substances but only a general class of substances which have a similar response under the same test conditions. "Total solids" may be found by taking the sum of the suspended and dissolved solids.

Specific conductance is the method of choice to determine dissolved solids. It is much more precise and economical. Ontario rivers and lakes free of industrial wastes have a dissolved solids equal to 0.65 ± 0.10 times the specific conductance.

Dissolved solids may be determined in three different ways therefore some caution must be exercised in interpreting the results. The calculation methods based on the conductivity and the summation of mineral components only considers dissolved "Ionic" solids.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
75 mls (3 ounces)	GLASS	None Required

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
50 mg/l - Unlimited (Gravimetric)	50 mg/l (Gravimetric)	± 25 mg/l (Gravimetric)

Dissolved solids are determined:

Gravimetrically on all industrial waste samples as well as any other type of sample where the specific conductance is greater than 400 micromohs/cm.

From Specific Conductance whenever the specific conductance is less than 400 micromohs/cm.

From the Sum of Constituents whenever Ca, Mg, Na, K, Cl, SO_4 , NO_3 , and alkalinity are all determined on a particular sample.

NOTE: Total solids will be substituted for dissolved solids only when filtration becomes impractical e.g. raw sludges digested sludges, mixed liquors, etc.

Time of Analysis

Two days are required to complete the gravimetric analysis. Samples are set up the first day and the weighing operation performed the second day. Approximately 75 samples may be set up per day.

FLUORIDE

Fluoride is beneficial in preventing dental cavities. The fluoride concentrations in domestic water supplies throughout Ontario are monitored to ensure that the M.O.E. objectives are met: 1 ± 0.2 mg/l for artificially fluoridated water and less than 2.4 mg/l for natural fluoride. The upper limit has been set because of possible tooth mottling.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
350 mls (12 Ounces)	GLASS OR PLASTIC	None Required

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
0.1 - 2.0 mg/l	0.1 mg/l	± 0.1 mg/l

The colorimetric alizarin method (Scott-Sanchis) is employed, based on the reaction between fluoride and a zirconium dye. High concentrations of aluminum and extreme conditions of pH cause interference effects. If such conditions are known to exist, a warning to laboratory staff will insure that the sample be distilled so as to eliminate these interferences. Warning when fluoride levels are expected to be greater than 20 mg/l are also appreciated in order to prevent the contamination of laboratory glassware with fluoride.

Colorimetric kits employed in water works laboratories can give slightly biased results if they have not been calibrated properly. Monitoring the actual dosage in pounds per hundred thousand Imperial gallons is most useful because by knowing the fluoride content of the water, a ratio may be established to relate the kit values to the actual known values such that an appropriate correction may be applied.

Time of Analysis

Approximately 100 samples may be analyzed per day if no pretreatment is required. Six samples may be analyzed per day if pretreatment by distillation is required.

FREE AMMONIA
(AMMONIA NITROGEN)

Ammonia nitrogen is a common substance normally encountered in domestic wastewater and industrial effluent. It is also found as a biochemical reduction product in ground water.

Ammonia nitrogen is undesirable because it is toxic to fish, exerts a high oxygen demand when converted to nitrite and nitrate, and interferes with water treatment procedures by reacting with chlorine to form chloramines. This reaction greatly reduces the disinfecting potential of the chlorination process. It is also objectionable because its nutritive properties promote the excessive growth of algae and other aquatic plants. Ammonia is rarely found in concentrations high enough to be harmful to humans.

Ammonia results are of great value in interpreting the effectiveness of the waste stabilization process at sewage treatment plants. The relative abundance of ammonia in the treated water is an indication of how far treatment has progressed.

Ammonia is rather short lived in surface waters, therefore it may not reveal the complete extent of pollution. Results must be interpreted with full allowance for its perishability, both in situ and in the sample following collection.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
75 mls (3 ounces)	GLASS OR PLASTIC	REFRIGERATE OR FREEZE

Ammonia is unstable and rapidly converted to other nitrogen compounds by bacterial activity. Samples must be refrigerated or frozen immediately after collection and delivered to the laboratory as soon as possible.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.02 - 2.0 mg/l	.02 mg/l	± .02 mg/l

Samples are pretreated by filtration and analysis is accomplished colorimetrically by the alkaline phenol hypochlorite method using an Auto Analyzer system. High levels of manganese, cobalt, iron, trivalent chrome, and calcium are known to produce interferences. Ammonia results are reported in mg/l of nitrogen.

Time of Analysis

Approximately 200 ammonia analyses may be performed during an 18 hour Auto Analyzer working period.

HARDNESS

The total hardness measures the "soap consuming power" of a water due to the presence of metallic cations. The principal components of the hardness are calcium and magnesium although a number of heavy metals may contribute to a small extent. The hardest waters are usually encountered in regions with thick topsoil layers and extensive limestone deposits.

Hard waters are objectionable because they form insoluble compounds or "curds" with soap. This substantially reduces the efficiency of washing procedures even when detergents are used. Larger quantities of soap are generally required for optimum cleansing in hard water, thus making the washing process considerably more expensive. Hardness in drinking water is limited indirectly by the criteria for dissolved solids.

Hardness has often been measured as a general indication of a water's mineral content. Waters with a high hardness are known to cause the formation of a lime scale in plumbing fixtures. It is therefore especially important to monitor the hardness of industrial water sources where high temperature equipment such as heat exchangers, boilers, steam turbines, hot water pipes, etc., are commonly employed.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
50 mls (2 ounces)	GLASS OR PLASTIC	None Required

Sample containers must be filled completely such that no air bubbles remain once they are capped. This precaution will prevent the loss of dissolved carbon dioxide which is essential for keeping any calcium carbonate in solution. Samples should not be refrigerated as this will cause the precipitation of calcium carbonate.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
6 - 500 mg/l	6 mg/l	± 2 mg/l

Samples are buffered to a pH of 10 and titrated with ethylenediaminetetraacetic acid (EDTA) to the Eriochrome Black T endpoint. Heavy metals interfere by masking this endpoint, however, suppression techniques are available. Results are reported in mg/l of calcium carbonate.

Time of Analysis

Approximately 70 hardness determinations may be completed per day.

IGNITED SOLIDS

Ignited solids refers to both the quantity of material that remains as a residue and the quantity of material that is lost when either the total, suspended, or dissolved solids residue is ignited at 600°C for one hour. The test does not determine specific substances but only a general class of substances which have a similar response under the same test conditions.

The loss on ignition is due to oxidation of carbon and hydrogen, escape of water of hydration, volatilization of inorganic ammonium salts, decomposition of magnesium carbonate, and loss of any other materials which are volatile or decomposable below 600°C. Thus, the loss on ignition generally overestimates the organic content. The actual organic content is lower by the amount of water, inorganic salts, etc., released. In the case of clean natural waters, the loss on ignition is due almost entirely to non-carbonaceous material therefore caution should be exercised in interpreting the results on such samples.

Ignited solids results are most useful in the characterization of sewage sludges where it is desirable to estimate organic composition. It is one of the major techniques used in assessing the efficiency of sludge digestion.

Any errors associated with the total, suspended, and dissolved solids determinations are also an integral part of the ignited solids result. Additional errors resulting from mechanical losses due to decrepitation are also a possibility.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
See Dissolved and Suspended Solids	GLASS	REFRIGERATE

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
100 mg/l-Unlimited	100 mg/l	Presently Not Available

Analysis is accomplished gravimetrically by taking the known total, suspended, or dissolved solids residue and igniting it at 600°C for one hour. Results are reported as mg/l of volatile solids and as mg/l of ash residue.

Time of Analysis

Approximately 75 ignited solids determinations may be completed per day.

TOTAL IRON

Iron is the most abundant of the heavy metals in nature, but despite this abundance, it is generally found at relatively low levels in natural surface waters. Iron is an important component of hemoglobin and an essential element for all life forms. It is non-toxic even at high levels but becomes objectionable in water because of the color and bitter taste it imparts. The water quality objective for Ontario drinking water is 0.3 mg/l as iron.

Iron exists in water as a variety of forms which include organic chelated complexes, inorganic chelated complexes, suspended hydroxides, suspended oxides, complex colloidal organics, ferrous ions and ferric ions. All of these forms are in a state of dynamic equilibrium therefore laboratory tests which attempt to differentiate between these various forms are not likely to produce values which are representative of field conditions at the time of sampling. For routine purposes, only a total iron determination is recommended.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
100 mls (4 ounces)	GLASS OR PLASTIC	A.A.S. - HNO_3 Colorimetric - HCl (10 Drop/Bottle)

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
A.A.S. .06 - 6.0 mg/l	.06 mg/l	± 0.1 mg/l
Colorimetric .05 - 2.0 mg/l	.05 mg/l	(At the 1.0 Level) $\pm .05$ mg/l

Routine low level irons are analyzed via the automated ortho-phenanthroline method. Samples are digested with hydrochloric acid and treated with hydroxylamine so that all the iron is converted to the ferrous state. Reaction of ferrous iron with orthophenanthroline produces an intense red colour which is proportional to the iron concentration. Interferences are not commonly encountered in natural waters, but any strong oxidizing agents, cyanides, nitrites, polyphosphates, chromium, zinc, cobalt, copper, and nickel are known to interfere. Non-routine industrial waste samples which contain elevated levels of heavy metals are analyzed for iron using atomic absorption spectrophotometry.

Time of Analysis

Approximately 175 analyses can be performed per day using the colorimetric method and 50 analyses per day using the atomic absorption method.

LEAD

Lead is found in nature chiefly as the mineral galena (lead sulfide) but also as cerussite, anglesite, crocoisite, wulfenite, pyromorphite, matlockite and vanadinate. Lead minerals and inorganic salts are relatively insoluble, thus the element most commonly enters a water supply via industrial, mine, and smelter discharges or through dissolution of lead in old corroded lead plumbing.

Lead is an extremely toxic element which tends to exchange with calcium and accumulate in bone marrow. Lead toxicity may not appear until many years after the last exposure. Organic compounds of lead are many times more toxic than inorganic forms. The most common example is tetraethyl lead which is used as an "antiknock" additive in motor fuels. Organic lead exerts its toxic effect on the nervous system within a very short time causing mental confusion, delirium, nausea, hallucinations, insomnia, and convulsions. The acceptable limiting concentration of lead in domestic water is 0.05 mg/l.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
100 mls (4 ounces)	PLASTIC	HNO ₃ (10 Drops/Bottle)

When levels below the normal range of application are required, a notation must be included on the sample submission form so that the sample may be preconcentrated prior to analysis. One full 32 oz. bottle is required exclusively for the preconcentration process.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
0.12 - 12 mg/l	.07 mg/l	± .09 mg/l (At the 1.0 Level)

A portion of the sample is digested in a nitric-hydrochloric acid mixture and analysis is accomplished by atomic absorption spectrophotometry.

Time of Analysis

Approximately 50 lead analyses may be completed per day.

LITHIUM

The element lithium is comparatively rare. It is concentrated in complex silicate minerals such as petalite and spodumene which are constituents of granite, nepheline syenite, pigmatites, and deposits of evaporate sediments. It is not often determined in routine water analyses, but has been found to be present in waters of hot springs, or highly mineralized brines, usually in amounts of less than 10 mg/l.

Lithium becomes toxic to animals and humans only if taken in very large amounts. When in sufficient quantity it has the capacity for replacing sodium in body cells, thus upsetting intracellular metabolism. Cause of death is generally due to kidney failure although secondary effects on the nervous system are also observed. Small doses of lithium carbonate have been effectively used as a sedative for treatment of psychiatric patients.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
100 mls (4 ounces)	PLASTIC	HNO ₃ (10 Drops/Bottle)

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.02 - 2.0 mg/l	.02 mg/l	± .06 mg/l (at the 2.0 Level)

Samples submitted for a lithium determination are digested in a nitric-hydrochloric acid mixture and analysis accomplished using atomic absorption spectrophotometry.

Time of Analysis

Approximately 50 lithium analyses may be performed per day.

MAGNESIUM

Magnesium ranks eighth in the natural order of elemental abundance and is commonly found in the minerals magnesite, dolomite, olivine, serpentine, talc and asbestos. Its industrial applications include the manufacture of metal alloys, photographic flash bulbs, flares, and tracer bullets.

Magnesium is present in all natural waters and generally associated with the presence of calcium. Only in rare instances is it ever found in greater abundance than calcium. If the magnesium concentration exceeds the calcium concentration, an artificial source is likely.

Magnesium is an essential element for the life functions of all plants and animals. It is closely associated with the metabolic activity of phosphorus where it is believed to act as an activator of phosphate enzymes. Ingestion of magnesium produces no adverse effects at levels normally encountered in domestic water supplies, but concentrations in excess of 125 mg/l exert a cathartic action on the gastro-intestinal tract.

Magnesium is a major contributor to water "hardness", therefore limitations on the amount of magnesium in water supplies is of concern especially to industry (see Hardness).

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
100 mls (4 ounces)	GLASS OR PLASTIC	None * Required

*Non-routine industrial waste samples or any other samples where high levels of heavy metals are suspected, should be sampled in plastic containers and preserved with 10 drops of nitric acid per bottle.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
Titrimetric - Unspecified A.A.S. .004 - 1.0 mg/l	-Unspecified .004 mg/l	-Unspecified ± .002 mg/l

Magnesium is most commonly determined by taking the difference between the calcium and the hardness levels and reporting this difference as mg/l of magnesium. Non-routine industrial waste samples, etc., are analyzed for magnesium using atomic absorption spectrophotometry.

Time of Analysis

Approximately 45 magnesium analyses may be completed per day using the titrimetric difference method and 50 per day using the atomic absorption method.

MANGANESE

Manganese is a common element in nature and found in numerous minerals which include pyrolucite, braunite, hauserite, manganese-spat, tephroite, knebelite, rhodomite, and many others. It is found at very low levels in natural waters, generally in the divalent (soluble) or quadravalent (suspended) state, but in the absence of dissolved oxygen the divalent state predominates. The permanganate anion, containing manganese in the heptavalent state, is not found in water unless it has been added artificially. High levels of manganese are usually the result of industrial discharges. Common industrial applications include the manufacture of metal alloys, dry cell batteries, paints, varnishes, inks, dyes, glass, ceramics, matches, fireworks, and fertilizer.

Manganese in trace quantities is essential for the proper nutrition of both animals and plants and is believed to be important in the metabolic oxidation-reduction processes of living cells. Manganese deficiency in animals is characterized by lack of growth, bowing and abnormal fragility of the bones, and degeneration of the reproductive organs. Manganese and its salts, ingested in very large quantities, are potent nerve toxins.

Although manganese is non-toxic at the levels commonly encountered in water supplies, it causes unpleasant tastes, stains laundry and plumbing fixtures, and encourages the growth of objectionable micro-organisms at treatment plants. Special techniques are often required to remove manganese. The maximum acceptable concentration of manganese for domestic water supplies in Ontario is 0.05 mg/l.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
100 mls (4 ounces)	PLASTIC	HNO ₃ (10 Drops/Bottle)

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.04 - 4 mg/l	.04 mg/l	± .01 mg/l (At the 0.2 Level)

Samples are digested in a nitric-sulfuric acid mixture and analysis is accomplished using atomic absorption spectrophotometry.

Time of Analysis

Approximately 50 manganese analyses may be completed per day.

MERCURY

Mercury is a relatively rare element commonly found as the mineral cinnabar (mercuric sulfide). It is seldom present in natural waters, the notable local exception being Lake Nipissing where natural deposits of cinnabar have elevated the levels of mercury in the water.

Mercury has many industrial applications which include the manufacture of barometers, thermometers, electrical switches, paints, pharmaceuticals, solders, disinfectants, biocides and fungicides. It is also used extensively in the production of caustic soda and chlorine. The presence of mercury in natural waters is likely the result of an industrial discharge.

The greatest environmental hazard associated with mercury is its tendency to become concentrated in living organisms. Any form of mercury entering an aquatic system could be converted via bacterial activity to methyl mercury derivatives. These substances will then become concentrated along a food chain until toxic levels begin to endanger higher forms of life. In man, mercury exerts its toxic effects on the nervous system. Common symptoms include muscular tremors, speech impairment, lack of co-ordination and emotional disturbances.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
250 mls (9 ounces)	GLASS ONLY (NO FOIL LINED CAPS)	HNO ₃ - KMnO ₄ (See Below)

Preservation is accomplished by adding 1 ml of concentrated nitric acid (Baker analyzed only) per bottle and enough potassium permanganate solution (saturated) to maintain a slight purple colour. Samples stored for over 3 days, even when preserved, may lose mercury. Immediate delivery to the laboratory is essential. Consultation with laboratory staff is advisable whenever mercury analyses are required.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.05 - 10 µg/l	.05 µg/l	± .03 µg/l (At the 0.2 Level) ± .14 µg/l (At the 8.8 Level)

Samples are first pretreated using a special acid digestion. Mercury vapor is then generated by the sequential addition of appropriate reducing agents and analysis accomplished via Flameless Atomic Absorption Spectrophotometry.

Time of Analysis

Approximately 20 mercury analyses may be completed per day.

MOLYBDENUM

Molybdenum is found in nature as the minerals molybdenite, wulfenite, and molybdenum ochre. Its industrial applications include the manufacture of steel alloys, glass, ceramics, pigments, lacquers, paints, electrical wiring, and fertilizer. It is also used as a catalyst in certain chemical processes. Its presence in natural waters is likely the result of industrial discharges.

In plants, molybdenum is believed to have an important influence on the ascorbic acid (vitamin C) equilibrium. It is essential to the nutrition of leguminous crops and all other nitrogen-fixing organisms. In animals, the function of molybdenum is not well understood but it appears to behave much like copper. It is known to be a constituent of certain flavoprotein enzymes which have essential metabolic functions.

Of all the industrial heavy metals, molybdenum is one of the least toxic. Isolated instances of molybdenum poisoning are generally associated with cattle grazing in pastures where the soil contains elevated levels of molybdenum (20-100 ppm). Normal soils contain between 3-5 ppm. This condition in cattle is commonly known as "teart" and is characterized by severe diarrhea, anaemia, and harsh discolored fur.

Molybdenum is rarely encountered in domestic water supplies and no limit has been specified for its maximum acceptable concentration.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
100 mls (4 ounces)	PLASTIC	HNO ₃ (10 Drops/Bottle)

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.03 - 10 mg/l	.03 mg/l	± .02 mg/l (At the 1.0 level)

Samples are pretreated by wet acid digestion and analysis is accomplished using atomic absorption spectrophotometry. The use of a high temperature nitrous oxide-acetylene flame and the addition of aluminum chloride at 2000 mg/l suppresses most interferences.

Time of Analysis

Approximately 50 molybdenum analyses may be completed per day.

NICKEL

Nickel is more abundant in Ontario than anywhere else in the world. It is found primarily as the sulfide minerals pentlandite, chalcopyrite, pyrrhotite, and nickelblende as well as the arsenic minerals kupfernickel and nickelglance. Nickel has numerous industrial applications, the most important of which is the manufacture of high quality, heat and corrosion resistant steel. Electroplating processes which utilize nickel are also widespread. Levels in natural waters are very low; therefore if nickel is found, it is likely the result of an industrial discharge.

Nickel and its salts have generally proven to be non-toxic to man even at very high levels. Nickel sulfate and nickel bromide have even been used therapeutically as a nervous sedative for headache, neuralgia, and insomnia. The notable exception is nickel carbonyl which is suspected of being carcinogenic, although confirmatory evidence is not well established. No maximum acceptable concentration in domestic water supplies has been specified.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
100 mls (4 ounces)	PLASTIC	HNO ₃ (10 Drops/Bottle)

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.07 - 7 mg/l	.07 mg/l	± .03 mg/l (at the 0.5 Level)

Samples are digested with a nitric-sulfuric acid mixture and analysis accomplished using atomic absorption spectrophotometry. Nickel is one of the elements most suited to atomic absorption analysis in that it is essentially interference free.

Time of Analysis

Approximately 50 nickel analyses may be completed per day.

NITRATE NITROGEN

Nitrates are formed via the oxidation of nitrite by autotrophic nitrifying bacteria and represents the most highly oxidized form of nitrogen in the nitrogen cycle. It is generally found at trace levels in all surface waters but may become very high in ground water as a result of soil leaching. Nitrate becomes a good substitute source of oxygen when the dissolved oxygen has been depleted.

Nitrates are objectionable because their nutritive properties promote the excessive growth of algae and other aquatic plants. Excessive amounts in drinking water contribute to a disease known as infant methemoglobinemia in which the oxygen carrying capacity of the blood is inhibited. The maximum acceptable level for domestic water supplies in Ontario is 10 mg/l of nitrate as nitrogen if the water is to be used for infant feeding. Nitrates are non-toxic to adults.

Nitrate results are of value in interpreting the effectiveness of the waste stabilization process at sewage treatment plants. Its abundance in treated water is an indication of how far treatment has progressed. Biochemical reduction of nitrate may frequently result in the production of nitrogen gas rather than ammonia (denitrification). This reaction is undesirable during the activated sludge process since the nitrogen gas tends to buoy the sludge and thereby inhibit digestion.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
75 mls (3 ounces)	GLASS OR PLASTIC	REFRIGERATE OR FREEZE

Nitrate is unstable and is rapidly converted to other nitrogen compounds by bacterial action. Refrigeration is helpful but freezing is the preferred form of preservation.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.02 - 2.0 mg/l	.02 mg/l	± .02 mg/l

Samples are pretreated by filtration and passed over granular metallic cadmium where nitrate is reduced to nitrite. Subsequent analysis for nitrite is accomplished colorimetrically (see nitrite nitrogen). High levels of hexavalent chrome, trivalent chrome, copper, iron and various oxidizing agents are known to cause interference effects. Results are reported as mg/l of nitrogen.

Time of Analysis

Approximately 200 nitrate analyses may be completed in an 18 hour Auto Analyzer working period.

NITRILOTRIACETIC ACID (N.T.A.)

The trisodium salt of nitrilotriacetic acid is presently being used as a replacement for phosphates in detergent formulations. This has caused widespread concern since the consequences of N.T.A. discharges to the environment have not been well established.

At present there is no adequate evidence to support the premise that N.T.A. is an environmental hazard. N.T.A. has proven to be relatively non-toxic as well as biodegradable. Degradation products which include CO_2 , H_2O , and inorganic nitrogen compounds are all safe naturally occurring substances. Of major concern is the possible interaction of N.T.A. with toxic trace metals. N.T.A. is a good chelating agent and may facilitate the transfer of toxic metals into biological systems over an extended period of time. Verification of this hypothesis may only be confirmed through long term studies.

Environmental monitoring of N.T.A. and research programmes attempting to define possible environmental hazards associated with N.T.A. are likely to become increasingly more important in the near future.

Sampling

Minimum Volume	Preferred Sample Container	Preservation Technique
600 mls (One Full 20 Ounce Bottle)	GLASS ONLY (20 ounces)	FORMALDEHYDE (2 mls/20 oz Bottle)

Submit one full 20 ounce glass bottle exclusively for N.T.A. analysis. Be sure to use caps with teflon liners.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.05 - 2.5 mg/l	.05 mg/l	Presently Not Available

Samples are analyzed directly using a dropping mercury polarograph. A gas chromatographic method and a colorimetric method are under development. Results are reported as the Acid.

Time of Analysis

Approximately 10 N.T.A. analyses may be completed per day by polarography.

NITRITE NITROGEN

Nitrite is present in natural water as an intermediary in the oxidation of ammonia by autotrophic nitrifying bacteria or in the anaerobic reduction of nitrate. In either case, its presence is short lived with the concentration seldom exceeding 1.0 mg/l as nitrogen. Higher concentrations are likely indicative of an industrial effluent. Waters containing nitrite are in the midst of rapid chemical changes.

Nitrite results may be used in interpreting the effectiveness of the waste stabilization processes at sewage treatment plants, but these results must be interpreted with full allowance for extreme perishability. The usefulness of nitrite results are questionable since it is highly unlikely that the concentration at the time of analysis represents the concentration at the time of sampling.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
75 mls (3 ounces)	GLASS OR PLASTIC	REFRIGERATE OR FREEZE

Nitrite is unstable and is rapidly converted to other nitrogen compounds by bacterial action. Refrigeration is helpful but freezing is the preferred form of preservation. Immediate delivery to the laboratory is essential.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.002 - 0.2 mg/l	.002 mg/l	± .001 mg/l

Samples are pretreated by filtration and analysis is accomplished colorimetrically via the diazotization reaction of nitrite with sulphanilic acid and 1-naphthylamine. The colorimetry portion of the procedure is performed automatically using an Auto-Analyzer system. High levels of iron, hexavalent chrome, and copper are known to produce interference effects. Results are reported as mg/l of nitrogen.

Time of Analysis

Approximately 200 nitrite analyses may be completed in an 18 hour Auto Analyzer working period.

PESTICIDES (CHLORINATED HYDROCARBONS)

Chlorinated hydrocarbon type pesticides are widely used in agriculture, industry, wild life control and public health programmes. Many of these materials are extremely stable and produce persistent residues in the environment. Biological accumulation of these residues in living cells are known to produce adverse effects on metabolic, enzymatic, neurological, and reproductive functions. Long term effects are not yet fully understood.

Samples submitted for the determination of CHLORINATED HYDROCARBONS will be analyzed for α BHC, β BHC, Lindane, Heptachlor, Aldrin, Dieldrin, Endrin, Heptachlor Epoxide, DDT, DDE, DDD, HCB and PCB's. The capability is available for analyzing many other classes of pesticides, herbicides, and slimicides, but these are generally considered non-routine. Consultation with laboratory staff is recommended when other substances are suspected.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
1000 mls (36 ounces)	GLASS ONLY (See Below)	REFRIGERATE (Store in the Dark)

One clean, solvent rinsed, 40 ounce glass bottle clearly labelled "PESTICIDES AND PCB's ONLY" should be submitted exclusively for this type of analysis. Plastic bottles should not be used under any circumstances as they will adsorb chlorinated hydrocarbons. Fill the bottle only to the top of the label leaving an air space of about 150 mls. Bottle caps must be foil lined as any rubber or plastic caps may release extraneous organic substances to the sample. Avoid the use of plastic or lubricated sampling devices.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
1.0 - 1000 ng/l (Dependent on Compound Analyzed)	1.0 - 20 ng/l (Dependent on Compound Analyzed)	$\pm 5 - 10\%$ (Dependent on Compound, Concentration and Interferences)

Pretreatment includes concentration by solvent extraction, column chromatographic cleanup, and separation into chemical classes. Identification and quantitative analysis is accomplished by gas chromatography.

Time of Analysis

Samples are generally set up in groups of ten per day, but the routine systematic analysis is extremely complex and requires five days to complete. When PCB's are present, special separatory techniques must be employed and analysis will take even longer.

PETROLEUM HYDROCARBONS

Petroleum hydrocarbons include gasolines, aviation fuels, organic cleaners, thinners (e.g. Varsol), kerosenes, stove oils, home heating fuels, diesel fuels, lubricating oils, cutting oils and transformer oils. Many of these substances may impart objectionable tastes and odours to domestic water supplies at very low levels. They are also known to increase the oxygen depletion rate in receiving waters and will hinder oxygen exchange with the atmosphere by forming slicks.

Petroleum hydrocarbons are generally found as a complex mixture of organic compounds. Identifications are therefore generally reported as a class or type of material rather than as a specific substance. In some cases a semi-quantitative measurement can also be provided. Laboratory staff should be consulted whenever a water contaminant requires source identification.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
900 mls (32 ounces)	GLASS ONLY	REFRIGERATE (See Below)

Open waters should be sampled at the surface as this is where petroleum hydrocarbons will collect. If closed plumbing systems are to be sampled, taps should not be opened for several hours prior to collection so that contaminants may build up. Tap sieves and toilet tanks are frequent areas where contaminants collect. Samples of the suspected contaminant source should be submitted with the contaminated water whenever possible.

One full 32 ounce bottle, clearly labelled "PETROLEUM HYDROCARBONS" should be submitted for this test exclusively. Bottle caps must be foil lined as any rubber or plastic caps may release extraneous organic compounds. Containers must be tightly capped and refrigerated to prevent the loss of volatile components. Petroleum hydrocarbons are susceptible to bacterial attack, therefore immediate delivery to the laboratory is essential.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
UNSPECIFIED	UNSPECIFIED	SEMI- QUANTITATIVE ONLY

An extraction is performed using an appropriate organic solvent and analysis is accomplished by gas chromatography.

Time of Analysis

Approximately 8 petroleum hydrocarbon determinations may be completed per day.

pH

pH is a measure of the hydrogen ion concentration in water. Specifically, it is the negative logarithm of the free hydrogen ion concentration expressed in moles per liter. Thus, each change of one unit in pH corresponds to a 10-fold change in the hydrogen ion concentration.

The pH does not measure the acidity or alkalinity. These parameters describe the buffering capacity of the water. Buffering capacity refers to the chemical constituents in the water that may take part in the neutralization of any artificially introduced acid or base without significantly changing the pH. The presence of an acidic or basic effluent in a natural water system will not necessarily be detected via a pH measurement. pH results are best interpreted in conjunction with the alkalinity and acidity.

Many organic dyes which change colour at a specific pH value are commercially available as "pH indicators". These dyes are appropriate for indicating reproducible pH's during titration procedures but are unreliable for the exact determination of an unknown pH. Use of these dyes are not recommended unless their limitations are fully understood.

pH is very dependent on temperature, dissolved gas concentrations, chemical reactions, etc., therefore it is one of the more perishable parameters determined. Field measurements are preferred if possible. Laboratory determinations are reported as "pH AT THE LAB" and must not be regarded as representative of the pH at the time of sampling.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
25 mls (1 ounce)	GLASS OR PLASTIC	None Required

Bottles should be filled completely so that no air bubbles remain once the samples are capped. For sludges use widemouth glass bottles and fill only half way. Do not refrigerate. Immediate delivery to the laboratory is essential.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
0 - 14 pH Units	Undefined	± 0.1 pH Units

pH is commonly determined using a potentiometer that is sold specifically for the measurement of pH. A good quality instrument is essential for precise measurements.

Time of Analysis

Approximately 100 pH measurements are routinely performed per day.

PHENOLICS (REACTIVE)

Phenolic substances are compounds having one or more hydroxy groups attached directly to an aromatic ring. This class contains a large number of compounds, but the term phenolic substance generally applies only to the simpler reactive phenol-like compounds which can be steam distilled at atmospheric pressure. Since phenol itself is used as a standard, it should be realized that phenolic substances are expressed as a phenol equivalent and represents the lowest possible value for phenolic content.

Phenolic substances in raw untreated waters are believed responsible for taste and odour problems in treated waters. Therefore, the maximum acceptable limit in the domestic water supplies of Ontario is .001 mg/l as phenol. Interpretation of the phenolic content is difficult, however, because some chlorophenols which may be formed during the chlorination process are not detectable. This then implies that a taste and odour problem due to the presence of chlorophenols may exist without any phenolic substances being detected. If more specific analytical information regarding phenolic content is required, laboratory staff should be consulted.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
Full Special Container	Special Glass Container	Special Container With Appropriate Preservative

Low level phenol samples are susceptible to bacterial attack and should therefore be refrigerated and delivered to the laboratory within 24 hours. Sampling is to be done in special bottles which already contain the proper amount of preservative. Preservation is not likely to be effective after 24 hours.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
4 - AAP 1 - 50 µg/l	1 µg/l	± 1 µg/l
GIBBS 2 - 120 µg/l	2 µg/l	Not Available

Samples for phenol analysis are acidified with phosphoric acid and distilled at approximately 120°C. Analysis is accomplished colorimetrically using the automated 4-aminoantipyrine method or the manual Gibbs method. Any organic substance which is steam distillable is a potential interference.

Time of Analysis

Approximately 60 phenol analyses may be accomplished per day using the automated 4-aminoantipyrine method and 30 per day using the Gibbs method.

POTASSIUM

Potassium ranks seventh in the natural order of elemental abundance. It is highly soluble and present at trace levels in all natural surface water, but very seldom exceeds 20 mg/l. Brackish or saline ground water, however, may contain potassium in excess of 100 mg/l. Potassium is generally found in the presence of sodium and only in rare instances will it ever exceed the sodium concentration. When potassium is in greater abundance than sodium, an artificial source is likely.

Potassium is an essential nutrient for all life forms, especially plants, and is therefore a major component of commercial fertilizers. It is non-toxic and represents no known health hazard. No limits have been specified for the maximum acceptable concentration of potassium in domestic water supplies.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
40 mls (2 ounces)	PLASTIC	None Required

Under alkaline conditions, glass containers are attacked releasing potassium ions to the sample. Pyrex is more resistant than soft glass, but plastic containers are preferred. Glass containers would suffice for sampling only when neutral pH conditions are known to exist.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
0.1 - 36 mg/l	0.1 mg/l	± 0.1 mg/l

Samples are analyzed using a flame photometer which relates the intensity of a characteristic potassium emission line to the intensity of known standards.

Time of Analysis

Approximately 70 potassium analyses may be completed per day.

SELENIUM

Selenium is found in nature as metallic selenides, selenites, and selenates, but also as organic compounds derived from decayed plant material. Its common industrial applications include the manufacture of rectifiers, photoelectric cells, red coloured glass, pigments, paints, dyes, and insecticides, as well as in the vulcanization of rubber as a supplement to sulfur.

Selenium is highly toxic, behaving in much the same manner as arsenic, and is believed to be a potentially carcinogenic agent. Selenium acts as an accumulative toxin in humans, causing rather vague symptoms such as gastric and nervous disturbances, dizziness, depression and fatigue. In cattle, selenium poisoning causes a condition commonly referred to as "blind staggers" or "alkali disease". Symptoms include impairment of vision, abdominal pain, partial paralysis, loss of hair, internal lesions and anemia. Some researchers have presented evidence to indicate that trace quantities of selenium are important as catalytic agents in the respiratory enzyme systems of living cells, but this has not been widely established.

Selenium is likely present in natural waters as the selenate anion ($\text{SeO}_4^{=}$) or as organic selenium compounds which have been discharged in industrial effluents. The maximum acceptable concentration of selenium for domestic water supplies in Ontario is 0.01 mg/l.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
100 mls (4 ounces)	PLASTIC OR GLASS	HNO_3 (10 Drops/Bottle)

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.002 - 0.2 mg/l	.002 mg/l	Presently Not Available

Samples are analyzed fluorometrically using 2,3-diaminonaphthalene. Analysis of selenium is an exceptionally lengthy process.

Time of Analysis

Approximately 5 selenium analyses may be completed per day.

SETTLEABILITY

Settleability describes that portion of sample which will undergo gravitational separation (settling) during a 30 minute time interval. It is commonly performed as a routine control procedure at sewage treatment plants, although it is occasionally performed by the laboratory branch for historical purposes.

The determination of settleability is a quick and easy empirical technique for evaluating the various stages of waste treatment. It is most valuable when performed at the treatment plant since visual qualities such as size, shape, and colour of the suspended particles as well as the optical properties of the supernatant are also observed during the analysis. Visual appearance may have more meaning in terms of treatment efficiency than the numerical value for settleability.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
900 mls (One Full 32 Ounce Bottle)	GLASS	None Required

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
0-1000 ml/l	Unspecified	Unspecified (Empirical Method)

A known volume of well mixed sample is poured into an Imhoff Cone and allowed to settle for 30 minutes. The volume of settled material is then related to the total volume of sample and the results reported in ml/l of settleable material.

Time of Analysis

One analysis may be completed in 30 minutes.

SILVER

Silver is found in nature as the native metal, but its chief source is the mineral argentite. Besides being relatively rare, most of its compounds are insoluble, therefore it is highly unlikely that silver would appear in a domestic water supply unless by artificial means. It is commonly used in the manufacture of silver utensils, jewellery, and solders as well as in the electroplating, photographic, and food processing industries. Exposure to silver in industry is usually manifested as a condition referred to as argyria; common symptoms include a permanent blue-gray discoloration of the skin and eyes. No recognizable disturbance of health need accompany this condition, although excessive exposure may result in kidney, liver, or spleen damage.

The maximum acceptable concentration of silver in domestic water supplies has been specified at .05 mg/l. This limit is used to restrict the use of silver compounds for disinfection and is indirectly based on public health considerations.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
100 mls (4 ounces)	PLASTIC	HNO ₃ (10 Drops/Bottle)

Samples should be analyzed as soon as possible after collection. Silver compounds are easily adsorbed on the walls of containers.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.04 - 4 mg/l	.04 mg/l	± .01 mg/l (At the 0.5 Level)

Samples are pretreated using a wet acid digestion and analysis is accomplished by atomic absorption spectrophotometry.

Time of Analysis

Approximately 50 silver analyses may be completed per day.

SLUDGE VOLUME INDEX

The sludge volume index (S.V.I.) is defined as the ratio between "settleability" in ml/l and the "suspended solids" in mg/l times one thousand. It is a measure of how well a sample settles and compacts. When the suspended solids are high, settling characteristics become negligible and compaction determines the sludge volume index. Generally an S.V.I. of less than 100 is considered indicative of a sludge with good compacting qualities.

The S.V.I. result is an empirical quantity with no assigned units. It is used by sewage treatment plant operators in determining when to increase or decrease the rate of sludge return.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
See Settleability and Suspended Solids	See Settleability And Suspended Solids	See Settleability and Suspended Solids

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
Unspecified	Unspecified	Unspecified

The settleability of a sample in ml/l is divided by the suspended solids in mg/l and the result multiplied by 1000. The sludge volume index is exclusively a calculated parameter dependent only on the settleability and the suspended solids (see settleability and suspended solids).

Time of Analysis

The time required to determine the S.V.I. is dependent on the time required to perform the settleability and suspended solids determinations.

SODIUM

Sodium ranks sixth in the natural order of elemental abundance and is characteristically the major ion in brackish or saline ground water.

Sodium is used extensively in the manufacturing of chemical products as well as in commercial water softening devices which employ the sodium ion-exchange process. It is generally abundant in all industrial effluents. Waters that receive surface drainage from roads during the winter season can also be very high in sodium, since sodium chloride is used to control road ice.

Sodium is an important element for all life forms and is generally considered non-toxic. However, patients with high blood pressure are usually warned to avoid the consumption of water containing more than 50 mg/l of sodium. Waters softened by the ion-exchange process employed in most domestic water softening equipment generally contains sodium in excess of this amount, thus the private use of this process should be practised with discretion.

Impairment of soil quality due to the presence of sodium is a major problem in agriculture. Soils high in sodium are generally characterized by low infiltration and permeability rates and are therefore unsuitable for farming.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
40 mls (2 ounces)	PLASTIC	None Required

Under alkaline conditions, glass containers are attacked releasing sodium ions to the sample. Pyrex is more resistant than soft glass, but plastic containers are preferred. Glass containers would suffice for sampling only when neutral pH conditions are known to exist.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
1 - 25 mg/l	1 mg/l	± 1 mg/l

Samples are analyzed using a flame photometer which relates the intensity of a characteristic sodium emission line to the intensity of known standards.

Time of Analysis

Approximately 70 sodium analyses can be completed per day.

SOLVENT EXTRACTABLES

The solvent extractable test measures the total quantity of substances present in a water sample that is readily soluble in an organic solvent. Such substances include fatty acids, petroleum products, oils and greases, resins, etc. They are generally found in effluents of oil refineries, meat packing plants, slaughter houses, dairies, canneries, and a variety of other industries.

Solvent soluble materials greatly increase the oxygen depletion rate in receiving waters and will hinder oxygen exchange with the atmosphere by forming slicks. Their presence is exceptionally troublesome in sewage treatment procedures where they are resistant to anaerobic digestion and accumulate within the digesters as scums.

The test does not measure the total organic concentration and if an identification is performed on the extracted material, it will not necessarily be representative of what was originally in the sample. Basic and volatile compounds for example, are not included in the determination. If anything other than a rough guide to the organic content is required, laboratory staff must be consulted.

Clear instructions must be given as to whether solvent extractables are required on the aqueous layer, the organic (oil) layer, or the total sample. Twigs, leaves, etc., are to be excluded as much as possible.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
900 mls (32 ounces)	GLASS	REFRIGERATE

One full 32 ounce bottle, clearly labelled "SOLVENT EXTRACTABLES ONLY", must be submitted for this test exclusively. Bottle caps must be foil lined as any rubber or plastic caps may release extraneous organic compounds to the sample. Do not use any chemical preservative. Solvent extractable substances are susceptible to bacterial attack, therefore immediate delivery to the laboratory is essential.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
2 - 100 mg/l (May be Extended Where Applicable)	2 mg/l	± 1 mg/l

An aliquot of the homogenized sample is acidified and extracted with a carbon tetrachloride/ethyl ether mixture. The solvent is then evaporated until the residue comes to a constant weight. The reported result is the residue weight in mg/l.

Time of Analysis

Approximately 10 solvent extractable determinations may be completed per day.

SPECIFIC CONDUCTANCE

The specific conductance is a measure of a water's capacity to carry an electric current. This property is related to the total concentration of ionized substances in the water. More formally it is defined as the reciprocal of a water's electrical resistance measured between two electrodes one square centimeter in area and one centimeter apart. A temperature change of 1°C will affect the conductance by about 2%, therefore all results are reported relative to a standard temperature of 25°C. The conductivity,* of natural waters is mainly due to the presence of calcium, magnesium, sodium, potassium, bicarbonate, chloride, sulfate, and nitrate ions. The conductivity contribution of the hydrogen ion is generally negligible for neutral waters, but begins to become significant at pH levels below 5.

Specific conductance relates quite well to the total dissolved solids concentration. Ontario rivers and lakes, free of industrial wastes, have a total dissolved solids generally equal to 0.65 ± 0.10 times the specific conductance. The conductivity* method for determining dissolved solids is presently used on a large number of natural water samples (see dissolved solids).

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
75 mls (3 ounces)	GLASS	None Required

Care must be taken to avoid contact with any material which can release or absorb ions. Samples should not be frozen as some carbonates are precipitated and not easily redissolved.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
$0.1 - 1.5 \times 10^7$ Micromohs/cm	0.1 micromohs/cm	$\pm 2 - 5\%$

The electrical resistance of the sample is measured by an instrument which takes the reciprocal automatically. A water bath is used to adjust the sample's temperature to 25°C before a measurement is taken.

Time of Analysis

Approximately 250 analyses may be completed per day.

* NOTE: "Specific conductance", and "conductivity" are often used synonymously.

STRONTIUM

Strontium occurs in nature as the minerals celestite, strontianite, and apatite. Natural compounds of strontium are relatively insoluble; therefore, its presence in domestic water supplies is generally very low. Possible industrial applications of strontium and its compounds include the manufacture of metal alloys, storage batteries, paints, rubber, cathode ray tubes, tracer bullets and flares. It's use, however, is not widespread.

Strontium closely resembles the chemical behaviour of calcium, tending to become concentrated in the human skeletal system. Strontium 90, the radioactive form which results from nuclear fallout, is included in the routine monitoring of radioactive components in Ontario's waters conducted by the Ministries of Environment and Health. No chemical limits have been specified as to the maximum acceptable concentration of strontium in domestic water supplies.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
100 mls (4 ounces)	PLASTIC	HNO ₃ (10 Drops/Bottle)

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.01 - 1.0 mg/l	.01 mg/l	Presently Not Available

Samples are prepared by a wet acid digestion and analysis accomplished using atomic absorption spectrophotometry. Interference by silica, zinc, aluminum, titanium, phosphate, and sulfate are suppressed by the use of lanthanum and a nitrous oxide-acetylene flame. Potassium nitrate is added to suppress ionization.

Time of Analysis

Approximately 50 strontium analyses may be completed per day.

SULFATE

Sulfate is an ionic component of all natural waters and is widely distributed in nature. It normally varies between 10 and 80 mg/l in most natural waters, but may go as high as several thousand mg/l when industrial discharges are involved. Rainfall may contain considerable amounts of sulfate if local industrial processes are emitting a sufficient quantity of sulfur dioxide and sulfur trioxide to the atmosphere. Sulfate tends to be exceptionally abundant in mine drainage wastes where it is produced via pyrite oxidation.

Waters high in sulfate tend to form hard scales in boilers, heat exchangers, and plumbing in general. Under anoxic conditions sulfates serve as an oxygen source for bacteria which convert it to hydrogen sulfide gas (hydrogen sulfide is recognizable by its characteristic odour of rotten eggs). Sulfate is also believed to be responsible for "crown" corrosion in concrete sewer pipes.

The maximum sulfate concentration specified as the objective for domestic supplies in Ontario is 250 mg/l. Concentrations above this level are non-toxic, but tend to exert a cathartic effect on the gastro-intestinal tract.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
50 mls (2 ounces)	GLASS OR PLASTIC	None Required

A non-routine modification has been developed to extend the detection limit down to 0.2 mg/l. Applications include rain water analysis and special studies. Laboratory staff should be consulted if low level measurements are required.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
1 - 50 mg/l	1 mg/l	± 1 mg/l

Sulfates are determined spectrophotometrically on an Auto Analyzer system using methyl thymol blue as the colorimetric reagent. No manual pretreatment steps are necessary. Interference effects occur when sulfide, sulfite, or any yellow coloured substances are present in the sample.

Time of Analysis

Approximately 80 sulfate determinations may be completed per day.

SULFIDE

Sulfide is formed by bacterial reduction of sulfate and organic sulfur compounds under anaerobic conditions. It is therefore commonly found in domestic wastewater, industrial wastewater, sludges, hypolimnions of stratified lakes and any other aquatic systems where anaerobic conditions prevail. Its characteristic odour of "rotten eggs" is highly objectionable.

Sulfide is an important parameter in waste treatment monitoring. Oxidation of sulfide to sulfuric acid by bacterial activity in concrete sewer pipes leads to "crown corrosion". Soluble sulfides in excess of 200 mg/l are toxic to bacteria and will inhibit sludge digestion.

Samples containing sulfides are unstable and results must be interpreted with caution.

Sampling

Minimum Volume of 900 mls	Preferred Sample Container	Preservation Technique
(One Full 32 ounce Bottle)	GLASS OR PLASTIC	$\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2\text{-Na}_2\text{CO}_3$ REFRIGERATE (See Below)

Samples must be collected with a minimum amount of agitation as sulfides are highly volatile and susceptible to oxidation by dissolved oxygen. Fill the container completely so that no air bubbles remain after the sample is capped. Immediate delivery to the laboratory is essential.

Preservation is accomplished by adding 2 mls of 2N zinc acetate solution to the sample followed by the dropwise addition of a 5% sodium carbonate solution until precipitation is complete. Preservation is not commonly practised on sewage type samples. Consultation with laboratory staff is recommended when sulfide analyses are required.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
Lead Acetate 0.1 - 5 mg/l	0.1 mg/l	Unspecified ± .02 mg/l
Molybdate .02 - 1000 mg/l	.02 mg/l	(At the 0.4 Level)

Samples are acidified and analysis accomplished colorimetrically using the lead acetate or the ammonium molybdate method. The lead acetate method is semi-quantitative and only used to obtain a rough estimate of the sulfide concentration. The molybdate method is much more precise and essentially interference free. However, organic sulfur compounds may release sulfide under the test conditions. Levels lower than those indicated above will be provided only on special request. Sulfide results are reported in mg/l as H_2S .

Time of Analysis

Approximately 60 sulfide analyses may be completed per day using the lead acetate method and 15 per day using the ammonium molybdate method.

SUSPENDED SOLIDS

Suspended solids refers to the quantity of material that may be removed from a water sample by filtration. The test does not determine specific chemical substances but only a general class of substances which have a similar response under the same test conditions.

The measurement of suspended solids is often improperly used in assessing water clarity. Clarity is a function of a water's optical properties and does not often relate to the quantity of suspended material present. Turbidity is a much better measurement of water clarity than the suspended solids, and in most cases should replace the suspended solids test.

Suspended solids are useful in evaluating the strength of domestic wastewater and in assessing the efficiency of waste treatment procedures. They are important in calculating loadings to aeration tanks, digesters, lagoons, sedimentation tanks etc.

Difficulty in taking a representative aliquot for analysis is probably the major source of error in the suspended solids measurement. Results on samples which contain large particles or more than 0.2% suspended material by weight are questionable because of rapid settling. In instances where the suspended solids visually appear less than 10 mg/l, the suspended solids test will be substituted by a turbidity measurement.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
200 mls (7 ounces)	GLASS	REFRIGERATE (Do Not Freeze)

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
3 - 1000 mg/l	5 mg/l	± 2 mg/l

Analysis is accomplished by filtering a known volume of sample through a preweighed filter paper (Reeve Angel 934 AH). The filter is then dried to constant weight at 103° - 106°C and results reported as mg/l of suspended solids.

Time of Analysis

Two days are required to complete the analysis. Samples are filtered the first day and the weighing operation performed the second day. Approximately 125 samples may be set up per day.

TANNINS AND LIGNINS

Tannins and lignins are members of a large group of hydroxylated aromatic compounds. They are natural components of plant material and are found in surface waters as a result of normal biochemical degradation processes, or as a result of industrial discharges. They are commonly found in the effluents of the paper and tanning industry. Tannins are also applied internally to boilers in order to facilitate the handling of calcium sludge deposits and to prevent the formation of a hard scale. Tannins and lignins are undesirable because they impart objectionable tastes and colours to domestic water supplies even at very low levels.

At present, no separations or individual determinations of tannins and lignins are performed at this laboratory. Results are standardized and reported as mg/l of tannic acid. To convert this result to a lignin number, the tannic acid value should be multiplied by 2.5.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
200 mls (7 ounces)	GLASS	Refrigerate Only

Since tannins and lignins are subject to normal biochemical oxidation, samples should be refrigerated to retard bacterial activity. No chemical preservation should be used as this may later interfere with the analysis. Immediate delivery to the laboratory is essential.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
1.0 - 10 mg/l	1.0 mg/l	± 1 mg/l

Tannins and lignins are determined colorimetrically by direct treatment with tungstophosphoric and molybdophosphoric acids (Tyrosine reagent). Any other reducing agent will produce the same color, therefore this test is not necessarily specific for tannins and lignins. Interference due to other reducing substances may cause an overestimation of the actual tannin and lignin content.

Time of Analysis

Approximately 40 tannin and lignin analyses may be completed in one day.

TITANIUM

Titanium is found in nature as the minerals rutile, ilmenite, and sphene. It ranks eighth in the natural abundance of elements and is readily found in most soils, varying between 0.5 and 10%. The high tensile strength and corrosion resistant properties of titanium metal are valuable in the manufacture of special steel alloys which are used for structural purposes in aircraft frames and engines. Titanium metal is also used in the manufacture of electrodes, lamp filaments, and x-ray tubes. Oxides of titanium are used as a white pigment in the paint, glass, and ceramics industries. Titanium and its salts are generally extremely inert and insoluble; the notable exception is titanium tetrachloride, which is highly corrosive.

There is no known toxicity to humans, animals, or plants. Surgical appliances are generally made of titanium and various titanium derivatives have been used in the treatment of skin disorders. No limits have been specified for the maximum acceptable concentration of titanium in domestic water supplies.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
100 mls (4 ounces)	PLASTIC	HNO ₃ (10 Drops/Bottle)

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.02 - 1 mg/l	.02 mg/l	± .02 mg/l

Samples are digested using a mixture of oxalic, sulfuric, and nitric acid. Final analysis is accomplished colorimetrically using Tiron (Disodium-1,2-Dihydroxybenzene 3,5-Disulfonate). This method is highly specific for titanium and interference effects are essentially negligible.

Time of Analysis

Approximately 20 titanium analyses may be completed per day.

TOTAL KJELDAHL NITROGEN

Total kjeldahl nitrogen is a measure of all the nitrogen in the trinegative state. It is primarily a measure of nitrogen present in the organic form, such as proteins, amines, urea, etc., but it also includes any nitrogen present as free ammonia. It does not include nitrogen present as nitrite or nitrate. "Organic nitrogen" can be obtained by taking the difference between the free ammonia and the total kjeldahl nitrogen results. "Total nitrogen" may be obtained by taking the sum of the nitrite, nitrate, and total kjeldahl nitrogen results. Kjeldahl nitrogen is used as an indicator of sanitary water quality.

Kjeldahl nitrogen results are of great value in interpreting the effectiveness of the waste stabilization process at sewage treatment plants. Treatment follows a natural sequence of biochemical reactions in which nitrogen components are successively oxidized from organic nitrogen, to ammonia, nitrite and finally nitrate. The relative abundance of each of these compounds in the treated water is an indication of how far treatment has progressed.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
75 mls (3 ounces)	GLASS OR PLASTIC	REFRIGERATE OR FREEZE

Kjeldahl nitrogen is a relatively stable parameter. Only oxidation of ammonia to nitrite and nitrate will influence the kjeldahl nitrogen perishability. This is not significant if the samples are analyzed within two or three days.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
0.1 - 2.0 mg/l	0.1 mg/l	± .05 mg/l

Samples are pretreated by digestion with sulfuric acid and potassium persulfate. Analysis is accomplished colorimetrically by the alkaline phenol hypochlorite method adapted to an Auto Analyzer system. High levels of manganese, cobalt, iron, trivalent chrome and calcium are known to cause interferences. Kjeldahl nitrogen results are reported in mg/l of nitrogen.

Time of Analysis

Approximately 200 samples may be analyzed during an 18 hour Auto Analyzer working period.

TOTAL PHOSPHORUS

Phosphorus occurs in natural and waste waters in several different combinations, which include orthophosphates, pyrophosphates, metaphosphates, polyphosphates and organically bound phosphates. Phosphorus is an essential element for all life forms and all of the above compounds may eventually be used in metabolic processes. Determination of the total phosphorus concentration is therefore more relevant than the measurement of individual phosphorus compounds.

Simple phosphates are used in the manufacture of fertilizers as well as detergents. Polyphosphates are used in some public water supplies and industrial boiler systems as a scale and corrosion inhibitor. Artificial inputs of phosphorus via wastewater and land run-off plays a significant role in promoting the overabundance of algae and aquatic plants which may impair water quality. Phosphorus results are generally used in assessing a water's potential for biological productivity as well as the efficiency of nutrient removal facilities at waste treatment plants.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
75 mls (3 ounces)	GLASS OR PLASTIC	REFRIGERATE OR FREEZE (See Below)

Contamination is a significant problem in the total phosphorus analysis. A rinse with 10% hydrochloric acid and distilled water is recommended to remove any trace of phosphorus from sampling containers. Refrigeration or freezing is required only if dissolved orthophosphate is to be determined on the same sample.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.005 - 0.2 mg/l	.005 mg/l	± .002 mg/l

Samples are pretreated by digestion with sulfuric acid and potassium persulfate and analysis accomplished colorimetrically using a phosphomolybdate technique which has been adapted to an Auto Analyzer system. High levels of silica, iron, trivalent chrome, hexavalent chrome, copper, zinc and various oxidizing agents are known to interfere. Results are reported as mg/l of phosphorus.

Time of Analysis

Approximately 200 samples may be analyzed during an 18 hour Auto Analyzer working period.

TURBIDITY

The turbidity is a measure of the optical properties of a sample which causes light to be scattered and absorbed rather than transmitted in a straight line. Historically, turbidity was measured using a Jackson Candle turbidimeter, but the insensitivity of this instrument led to the development of secondary techniques which can measure the much lower turbidities commonly encountered in modern water treatment processes. The instrument currently employed at the laboratory is fundamentally different in optics and cannot be validly calibrated against the Jackson Candle turbidimeter.

Clarity is one of the main criteria which the public uses in judging water quality, either for drinking or for recreational use. This makes the measurement of turbidity a much more valuable gauge of water quality than the suspended solids test, which measures only the weight of particles present in suspension and has little direct bearing on the appearance of the water. It is recommended that field staff make greater use of turbidity in place of suspended solids measurements.

Care must be used in interpreting turbidity results since these are defined by the instrument, the standards and the optical phenomena being measured. Standards other than Formazin are exceedingly difficult to reproduce since their optical properties depend on the size, shape, and refractive index of the component particles in suspension.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
50 mls (2 ounces)	GLASS OR PLASTIC	KEEP IN DARKNESS

Samples should be stored in darkness and delivered to the laboratory within 24 hours.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.05 - 1000 FTU	.05 FTU	± 2%

Light scattered by the sample at $90^\circ \pm 30^\circ$ is measured in a nephelometer calibrated with Formazin standards. Results are reported in Formazin Turbidity Units (FTU). Rapidly settling particles, gross debris, or dissolved colored substances may invalidate the results.

Time of Analysis

Approximately 150 turbidity determinations may be performed per day.

URANIUM

Uranium is found in nature as the mineral carnotite as well as in igneous type rocks. It is well known for its radioactive properties since its major industrial application is the manufacture of nuclear fuel. Natural uranium, however, is present as the isotope U^{238} , which is not strongly radioactive and does not represent a significant health hazard.

In natural waters uranium is hexavalent and commonly present as the uranyl ion UO_2^{++} . Uranyl salts are all very soluble and produce an objectionable taste and colour when they exceed a concentration of 10 mg/l as uranium. At considerably higher levels, ingestion of water containing uranyl ions may result in possible kidney damage. Limits on the maximum concentration of uranium in domestic water supplies, when specified, are generally based on chemical properties of the uranyl ion rather than on radioactivity.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
100 mls (4 ounces)	PLASTIC	HNO_3 (10 Drops/Bottle)

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.01 - 1.0 mg/l	.01 mg/l	Presently Not Available

Samples are pretreated with granular zinc to reduce all uranium to the proper valency. Analysis is then accomplished colorimetrically using ARSENAZO III.

Time of Analysis

Approximately 10 uranium analyses may be completed per day.

VANADIUM

Vanadium occurs in nature as the minerals vanadinite, patronite, mottramite, and carnotite, and is generally found in the presence of selenium. It is most valuable in the steel industry where it is known to increase the general toughness and tensile strength of certain alloys, but it is also used in the manufacture of dyes, paints, inks, ceramics, as well as in the photographic industry. The presence of vanadium in natural waters is likely the result of industrial discharges.

The usefulness of vanadium in animal and plant metabolism has not been convincingly demonstrated and its behavior in biological systems is not well understood. Some experimental evidence suggests that the presence of vanadium in trace quantities may be beneficial in the prevention of heart disease.

Several compounds of vanadium are known to be toxic in high concentration. Exposure may produce nausea, diarrhea, abdominal pain, nervous trembling of the hands, and greenish-black discoloration of the tongue. No limits have been specified for the maximum concentration of vanadium in domestic water supplies since the element is rarely encountered.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
100 mls (4 ounces)	PLASTIC	HNO ₃ (10 Drops/Bottle)

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.04 - 4.0 mg/l	.04 mg/l	Presently Not Available

Samples are pretreated using a wet acid digestion followed by oxidation with potassium permanganate. Analysis is accomplished colorimetrically using sodium tungstate as the colour producing reagent. This method is subject to a number of interferences.

Time of Analysis

Approximately 20 vanadium analyses may be completed per day.

VOLATILE ACIDS

Low molecular weight organic acids which are readily distilled from aqueous solution at low temperature are commonly called volatile acids. They include acetic, propanoic, and butanoic acids as well as small amounts of valeric, isovaleric, and caproic acids. These volatile acids are formed as intermediates during the anaerobic degradation of carbohydrates, proteins and fats in sludge treatment processes. An excess accumulation of these acids can have a deleterious effect upon anaerobic digestion. In routine operation of an anaerobic waste treatment system, the volatile acid concentration is primarily used as the determining and controlling factor for a satisfactory balance between the saprophytic and methane producing bacteria which are largely responsible for the efficiency of anaerobic digestion.

Volatile acids are found in natural waters when anoxic conditions are prevalent, but they are extremely unstable and would not likely be found in domestic water supplies.

Results are reported as mg/l of acetic acid.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
25 mls (1 ounce)	GLASS	REFRIGERATE

Sludges should be collected in wide mouth glass jars and not filled more than half-way. Volatile acids are extremely unstable, therefore they should be maintained at 4°C and delivered to the laboratory immediately.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
50 - 2500 mg/l	50 mg/l	± 25 mg/l

Volatile acids are separated by means of a column chromatographic technique using a chloroform-butanol elutant. The eluate is then titrated with standard alcoholic sodium hydroxide to the phenolphthalein endpoint. This procedure is capable of eluting higher molecular weight organic acids as well as some synthetic detergents, however, the concentration of these substances are generally negligible in sludges.

Time of Analysis

Approximately 20 volatile acid determinations may be completed per day.

ZINC

Zinc is commonly found in nature as zinc sulfide in the mineral sphalerite and as zinc carbonate in the mineral calamine. It is widely used in the manufacture of metal alloys such as brass, batteries, dyestuffs and paints, as well as in electroplating. Zinc most commonly enters a water supply via the deterioration of galvanized iron, the dezincification of brass, and direct industrial discharges.

In plants, zinc has been found to be an essential nutrient for normal growth. Plants growing in a zinc deficient soil are severely stunted. In animals, zinc has been found to be an important constituent of a number of enzymes, notably carbonic anhydrase, which is vital for normal respiration. Zinc and its compounds are relatively non-toxic when taken orally. Even at high concentrations, nausea and diarrhea are the only adverse effects likely to be encountered. The limiting factors which determine the acceptable maximum concentration in a water supply are taste and appearance. Zinc, in excess of 5 mg/l, imparts a bitter astringent taste; a milky, opalescent appearance and may cause a greasy film when the water is boiled. The maximum acceptable limit for domestic water supplies in Ontario is therefore 5 mg/l.

Sampling

Minimum Volume of Sample	Preferred Sample Container	Preservation Technique
100 mls (4 ounces)	PLASTIC	HNO ₃ (10 drops/bottle)

Preconcentration is necessary if lower levels are required. In this event, submit a full 32 oz. bottle exclusively for zinc analysis.

Method

Range on Undiluted Sample	Detection Limit	Precision (Standard Deviation)
.05 - 5 mg/l	.05 mg/l	± .05 mg/l (at the 0.5 Level)

Samples are digested with a nitric-sulfuric acid mixture and analysis is accomplished using atomic absorption spectrophotometry. Very high (0.5%) levels of calcium, sodium, or potassium can interfere with the zinc analysis. If the presence of such species are suspected, the laboratory should be informed.

Time of Analysis

Approximately 50 zinc analyses may be completed per day.

BIBLIOGRAPHY

- 1) Standard Methods for the Examination of Water and Wastewater, 13th Edition, APHA (1971).
- 2) Klein, L., Chemical Aspects of River Pollution, Butterworth (1962).
- 3) Sawyer and McCarty, Chemistry for Sanitary Engineers, 2nd edition, McGraw-Hill (1967).
- 4) Browning, E., Toxicity of Industrial Metals. Butterworth (1961).
- 5) Report of the Committee on Water Quality Criteria, Federal Water Pollution Control Administration, U.S. Dept. of the Interior. (1968).
- 6) Crosby, Dennis, and Stevens. An Evaluation of Some Methods for the Determination of Fluoride in Potable Waters and other Aqueous Solutions. Analyst 93, 643 (1968).
- 7) Rigler, F.H., The Phosphorus Fractions and the Turnover Time of Inorganic Phosphorus in Different Types of Lakes. Limn. and Ocean. 9, 511 (1964).
- 8) Fitzgerald, G.P., and Faust, S.L., Effect of Water-Sample Preservation Methods on the release of Phosphorus from Algae, Limn. and Ocean. 12, 332 (1967).
- 9) Methods for Chemical Analysis of Water and Wastes, U.S. Dept. of the Interior, FWPCA (1971).
- 10) Traversy, W.J., Methods for Chemical Analysis of Waters and Wastewaters, Canada Dept. of Fisheries and Forestry, Water Quality Division, Inland Waters Branch (1971).
- 11) Kopp, J.F. and Krones, R.C. Trace Metals in Waters of the United States, U.S. Dept. of the Interior, FWPCA, Division of Pollution Surveillance (1967).
- 12) Hem, J.D., Study and Interpretation of the Chemical Characteristics of Natural Water, U.S. Dept. of the Interior, Geological Survey (1965).
- 13) Parker, C.R., Water Analysis by Atomic Absorption, Varian Techtron PTY. Ltd. (1972).
- 14) Drinking Water Objectives, OWRC, (1967).

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